# MATERIA PHOTOGRAPHICA BY CLEMENT J. LEAPER



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MATERIA PHOTOGRAPHICA.



# MATERIA PHOTOGRAPHICA:

A TREATISE ON THE

# MANUFACTURE, PROPERTIES,

AND USES OF THE

# SUBSTANCES EMPLOYED IN PHOTOGRAPHY.

BY

# CLEMENT J. LEAPER, FC.S.,

Honorman, Medallist and Prizeman in Photography City and Guilds of London Technical Institute.

Instructor in Photography and Chemistry City of Dublin Technical Schools.

Author of "I hotography for Fun," "Experimental Fhotography," "Construction and Use o Photographic Lenses," "Synoptical Tatles of Inorganic and Organic Chemistry," etc., etc.,



**>+**<

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# PREFACE.

THE origin of this volume was the course of instruction in photography annually given by me at the City of Dublin Technical Schools, during which a demand repeatedly arose for a work of this kind. I cannot, of course, boast of much originality, my task resolving itself for the greater part into the selection of suitable material. This has been taken from the works, etc., mentioned in the Bibliography, to the authors of which I beg to tender my sincere thanks.

My best thanks are also due to my publishers, for the exceptional facilities they have afforded me in the matter of illustrations, and to one or two friends who have helped me with valuable suggestions.

In spite of every care, I fear that numerical and other errors may have found their way into the work, and as these would materially detract from its utility, I appeal to my readers to communicate any apparent discrepancy they may find either to my publishers or to myself, so as to enable it to be set right in subsequent editions.

CLEMENT J. LEAPER.

4, Chester Road, Dublin, June, 1891.

# ERRATA.

```
27, line 28 from top, for "discoloured" read "decolourised."
Page
                            for "+40°C" read "- 40°C."
       31, ,,
               26
  ,,
                            for "hydrochlorate"
       34, ,,
               21
                                                    read
                                                           "hvdro-
  ,,
                                   chloride."
       42,
                3 from bottom, for "sulphuric"
                                                    read
                                                           "hvdro-
                                   chloric."
       46, ,,
                5
                                for "redistilling it over"
  ,,
                                   "shaking it up with."
               27 from top, for "oxalate" read "oxalic."
       71, ,,
  ,,
               12 from bottom, for "paper" read "powder."
       73,
  ,,
                               for "tubular" read "tabular."
       95, ,,
               18
  ٠,
               18 from top, for "hydrobiomic" read "hydriodic."
       96,
  ,,
               8 from bottom, for "potash is formed" read "pot-
      116.
                                  ash and soda are formed."
      116, ,,
                                     "potassium oxalate"
               12
                                  "potassium and sodium oxalate."
      116
               8
                               for "caustic potash is" read "caustic
                       ,,
                                  soda and potash are."
               3 from top, for "malted" read "melted."
      121
              21 from bottom, for "pante" read "ante."
      121
                               fer "hypo" read "pyro."
      125
              19
  ,,
      145
              18
                               for "mixable" read "miscible."
                               for "iodide" read "cvanide."
      148
              16
  ,,
                               for "tatropha" read "jatropha."
      166
               1
                               for ",188-201)" read ",190-191-204)"
              15
      182
  ,,
                               for "(190·191 203)" read "(192·193)"
      182
              19
  ,,
                               for "(242)" read "(245)"
      192
  ,,
               8, 10 & 12 from bottom, for "136" read "140."
      197
  11
               9 from top, for "(201)" read "(35-204)"
      201
  ,,
                           for "(203)" read "(194·195)
      201
              17
  ,,
                           for "(191)" read "(183 188)"
      202
  ,,
               7 from bottom, for "groined" read "translucent"
      207
  ,,
              6 & 7 from top, delete "hot varnishes for ferrotypes."
      209
                                for "we therefore measure out
      230
               11 & 12
  ,,
                                   this quantity" read "we there-
                                   fore measure out more than this
                                   quantity, say 100 cc."
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# MATERIA PHOTOGRAPHICA.

### INTRODUCTION.

Whilst photographic literature is being enriched almost daily by books describing the *technique* of the science, works dealing with the preparation and properties of the substances employed therein are comparatively scarce, and even such manuals of the kind which we possess deal with this branch of photography in a very cursory manner.

To supply this want I have undertaken the present articles. How far I shall succeed in my object remains yet to be seen, but I may say, without egotism, that I shall endeavour to present as a consecutive whole what hitherto could only be found by searching through dozens of volumes.

I shall assume throughout, on the part of my readers, a general knowledge of theoretical chemistry (without which, indeed, it is impossible to practice photography in anything but a haphazard manner), and sufficient manipulative dexterity to enable them to conduct simple chemical operations.

Materia photographica is to photographers what materia medica is to physicians and pharmacists, viz., a description of the methods of preparing, testing, and using the various substances they employ.

Of the importance and utility of such knowledge it is almost unnecessary to speak. To the photographer who resides in distant lands, and even to the resident in out of the way places at home, to know how to make what they cannot possibly procure must be of paramount interest, and even dwellers in cities will find it instructive to be able to test their purchased chemicals for impurities, and thus perhaps obtain a clue to the cause of unexpected failures.

The subject is conveniently subdivided into five parts:—

- I.—Apparatus and reagents and their uses.
- II.—Photographic chemicals.
- III.—Photographic formulæ.
- IV.—The utilisation of photographic so-called wastes.
  - V.—Quantitative chemical analysis applied to photography.

# PART I.

### APPARATUS AND REAGENTS AND THEIR USES.

Without professing to be by any means exhaustive, the list given below will be found to include everything necessary for ordinary requirements.

To begin work, some source of heat, such as a spirit lamp or Bunsen burner, a test tube stand and test tubes, and a few flasks and funnels will suffice; the remaining apparatus can then be purchased as occasion demands. The work-room or laboratory should be, if possible, a room set apart for that purpose, and in which no photographic operations are conducted. Failing this, a small cupboard may be provided in the dark-room to hold chemical apparatus and chemicals but, with respect to the latter, special care must, in that case, be taken rigidly to exclude solutions of sulphuretted hydrogen and of chlorine, which would play sad havoc with plates and paper, and when performing any operation involving the production of any gas, all photographic plates and papers must for the time being be removed.

The following laboratory hints will prove useful to beginners:— Have a place for everything, and, when done with, return every

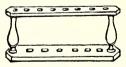
thing to its place.

Clean your apparatus immediately after use.

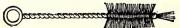
Perform every experiment as carefully as possible, and attentively observe the result.

Make careful notes of everything you do.

THE CONTENTS OF THE WORK ROOM.

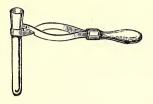


Test Tube Stand and Test Tubes.—The stand is made of hard wood, and pierced with six or more holes, which support tubes of thin glass, closed at one end. Tubes about 6 × ½in. are most suitable.



Test Tube Brush.—This consists of twisted wire covered at one end with bristles. It is used to clean out tubes, &c. Care should

be taken to wash out the tube, &c., with water before using the brush, so as to avoid corroding the iron with acid solutions.



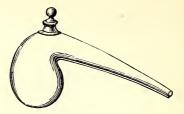
Test Tube Holder.—A clip for holding hot test tubes. A piece of paper folded four times upon itself, and wrapped round the tube, answers as a makeshift substitute.



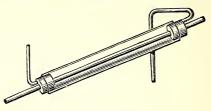
Beakers are vessels shaped somewhat like drinking glasses, but made of very thin and hard glass. Wide beakers are more convenient in every way than narrow ones. They are generally sold in various sized sets. A set of five beakers ranging from 5oz. to 16oz. capacity is a serviceable one.



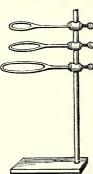
Flasks.—Glass vessels for heating liquids, etc. Those conical in shape are easier cleaned, and preferable in every way to the old globular pattern. Empty Florence oil flasks are useful for certain purposes. They can be readily freed from oil by washing them with soda and slaked lime.



Retorts are thin glass globes, with bent necks, and intended to receive liquids for distillation. Tubulated retorts are far more convenient than plain retorts, but, of course, more expensive. For many purposes a flask, or even an ordinary tin can fitted with a cork and a bent glass tube, answers instead of a retort.



Liebig's Condenser consists essentially of an inner glass tube, surrounded by an outer one, through which water circulates. It is employed for distillations, the vapour it is required to condense being led through the inner tube.



Retort Stand.—This is a vertical iron rod, mounted on a heavy metal foot, and provided with rings which slide up and down, and can be clamped in any desired position by thumbscrews. The rings are employed for holding basins, retorts, etc., which are being heated.



Evaporating Basins are shallow vessels of thin porcelain, glazed inside, and intended to hold liquids which are being evaporated. Those made of Dresden porcelain are least liable to crack, but are more expensive than other varieties.



Tripod—A piece of apparatus sufficiently described by its name and serving to support basins, etc. It answers, in fact, most of the purposes of a retort stand.

Wire Gauze.—Several pieces 4in. square, and made of stout iron wire with meshes  $\frac{1}{10}$ in. apart will be required. These are placed on the tripod or retort stand, and serve to support beakers and flat-bottomed flasks.

Glass Funnels.—Several of these, from 1in. to 6in. in diameter, will be needed. Plain, not ribbed, funnels should be chosen.

Filter Papers are circular discs of white bibulous paper, sold in packets of 100, and of various sizes to suit the funnels. Filter papers are  $1\frac{1}{2}$  times the diameter of the funnels they are intended to suit, thus a 3in. paper will fit a 2in. funnel, etc.



Thistle Funnels are glass tubes provided with a small funnel at the top. The tube should be about 12in. long and ½in. external diameter.

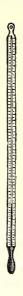


Mortar and Pestle.—This should be of stout German porcelain, unglazed within, and provided with a pestle in one piece. When soiled friction with soap and pumice-stone will readily clean it.

Glass Covers.—Thin shallow clock glasses are best, but flat glass plates (rejected negative glasses) will do. They are used to protect the contents of beakers from dust.

Watch Glasses.—Several of these should be provided for experiments on a small scale with expensive materials.

Crystal Drainer.—A porcelain basin pierced with numerous fine holes, and serving to drain crystals from the adhering liquid.



Chemical Thermometer.—A thermometer is used for measuring temperatures, and this variety of the instrument differs from those in ordinary use in having the scale enclosed in a glass tube so as to enable it to be immersed in liquids. A narrow thermometer should be selected, with a milk-glass scale graduated from 10° to 200° C. Some instruments are made with Centigrade scale on one side and Fahrenheit on the other, and are very convenient, but expensive.

Corks, Rubber.—Red rubber ones should be selected to fit flasks from five to sixty ounces capacity.

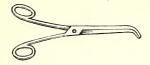
Cork Borer consists of a series of thin brass tubes, sharpened to an edge at one end and fitting one inside the other. They are employed to pierce ordinary or rubber corks, for which latter purpose they must be moistened with water, or, better, with alcohol.



Crucibles are vessels of fireclay, porcelain, &c., intended to hold dry substances which are to be subjected to an intense heat. The larger ones are heated in a clear fire or special furnace, the smaller ones over a burner or spirit lamp.



Pipeclay Triangle consists of a wire triangle, on which three pipe-shanks are threaded, and serves, supported on the ring of the retort stand, to hold small crucibles.



Crucible Tongs are made of iron or brass, and employed to hold hot crucibles.

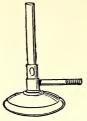
Glass Tubing.—An assortment of this will be required. That  $\frac{1}{4}$  in. to  $\frac{5}{16}$  in. external diameter and thin in the walls is most easily worked.

Rubber Tubing.—Pure red or black tubing, although dearest at first, is cheapest in the end, as it lasts much longer than the cheaper white varieties. It must be chosen to suit the glass tubing.

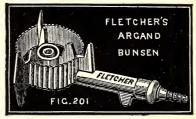
Glass Rod.—This is sold in lengths, and by weight. That  $\frac{3}{16}$  in diameter is best for most purposes.

Triangular File.—Useful for marking glass tubing and rod previous to breaking.

Platinum Wire.—One or two pieces about  $2\frac{1}{2}$ in. long by  $\frac{1}{16}$ ir, in diameter will be required.



Bunsen's Burner consists of an upright metal tube, through which coal gas passes, whilst at the bottom are openings for the supply of air. It is very useful for heating crucibles, but is apt to localise the heat too much when used with beakers, flasks, etc., for heating which the next burner is more suitable.



Solid Flame Burner is really a flat Bunsen, and most useful for almost every purpose, except, perhaps, heating crucibles.



Spirit Lamp.—Where gas is not available this must be employed instead of the preceding. Care should be taken that methylated spirit, not finish, is employed with it, otherwise a smoky flame will result.



Wash Bottles are ordinary wide-mouthed bottles fitted (as shown

with an indiarubber cork and tubes. Flasks, except where the contents have to be heated, are quite unnecessary.



Sulphuretted Hydrogen Apparatus consists of two twenty ounce bottles fitted (as shown) with rubber corks and tubes. To generate the gas, ferrous sulphide, in small pieces, is placed in the one carrying the thistle funnel, and a little water in the other. A rubber tube is then slipped over the exit tube, and a glass tube passed into this, and caused to dip beneath the surface of the liquid through which it is desired to pass the gas. Finally, a cold mixture of one volume commercial oil of vitriol and four volumes water is poured down the thistle funnel, when the gas is evolved in abundance. The whole operation is best performed out of doors, on account of the intolerable smell of the sulphuretted hydrogen.

Corks Ordinary, Graduated Measuring Glasses, Scales and Weights.

—These call for no special remarks.

# REAGENTS FOR QUALITATIVE ANALYSIS.

The following list includes the ordinary reagents. Special ones will be described as required:—

Liquids.—(1.) Sulphuric acid, strong, pure. (2.) Nitric acid, ditto. (3.) Hydrochloric acid, ditto. (4.) Acetic acid. (5.) Sodium hydroxide. (6.) Ammonium hydroxide. (7.) Sodium acetate. (8.) Ammonium sulphide. (9.) Ammonium carbonate. (10.) Ammonium chloride. (11.) Ammonium oxalate. (12.) Potassium chromate. (13.) Potassium iodide. (14.) Potassium ferrocyanide. (15.) Silver nitrate. (16.) Barium nitrate. (17.) Lead nitrate. (18.) Calcium sulphate. (19.) Calcium hydroxide. (20.) Tartaric acid. (21.) Sulphuretted hydrogen. (22.) Sodium phosphate.

Solids.—(23.) Starch. (24.) Ferrous sulphate. (25.) Copper tacks. (26.) Litmus papers, blue and red. (27.) Manganese peroxide. (28.) Potassium ferricyanide.

The liquids are best kept in stoppered bottles, but corked bottles will do for all but the first six. Light green glass is the best and cheapest material, being far less liable to be corroded by reagents than white glass.

Each bottle should be distinctly labelled. Printed labels are sold for that purpose, to prevent which from being rubbed off it is well to size them with gelatine, after sticking them on the bottles, and then to coat them with a solution of 20 grs. of mastic in an ounce of ether.

The solutions contain in 10 ounces of water the undermentioned weights of their respective solids:—Nos. 5, 10, 12, 14, 22, one ounce; Nos. 11, 13, 15, 16, 17, half-ounce; Nos. 18 and 19, six grs.; No. 7, three ounces.

No. 20 is made by dissolving, by the aid of heat, five ounces of the solid in five ounces of water, and adding to the solution 20 grs. of salicylic acid dissolved in half-an-ounce of alcohol. No. 21 is a saturated solution of the gas in water, made by passing it through the liquid until no more is absorbed. No. 8 is made by saturating an ounce of strong ammonia with sulphuretted hydrogen, and adding to this eight ounces of water and another ounce of strong ammonia. No. 9 is made by dissolving two ounces of the solid in ten ounces of cold water, and adding two ounces of strong ammonia. No. 4 contains a fluid ounce of glacial acid mixed with ten ounces of water. No. 6 three fluid ounces of strong ammonia mixed with ten ounces of water. Nos. 1, 2, and 3 and the solid reagents are used as purchased.

Distilled water should be employed in making up the solutions, which must when made be quite clear. If they are not they should be carefully filtered.

The stopper of No. 5 (sodium hydroxide) is very liable to stick fast, but this can be obviated by smearing it occasionally with a little vaseline. All the solutions keep well but No. 21 (sul phuretted hydrogen). This can rarely be relied on longer than a fortnight after preparation.

The quantities of solutions to be made up will depend, of course, upon the amount o work expected to be done. Five ounces of the liquids and an ounce of the solids are quantities quite sufficient to start with, and will last for some time.

### MANIPULATIONS.

Operations having for their object the preparation, testing, &c., of chemical products are termed chemical manipulations. The more important of these are classified below.

1. Solution.—This is the intimate mixture of any solid, liquid or gaseous substance with a liquid. The term is used indifferently, and perhaps erroneously, to denote a process, as the dissolving of washing soda in water, by which the properties of the dissolved substance are unchanged, and one, as in adding washing soda to hydrochloric acid, which yields a totally new product.

A solution is said to be saturated when it contains as much as possible of the substance. With solids, as a general rule, the higher the temperature the more will it be found possible to dissolve. With gases, however, the opposite holds good. A saturated solution of a gas in water, say the ordinary solution of ammonia, will, on the temperature being raised, liberate more or less of the gas.

With solids, sub-division promotes solution; hence many solids are directed to be powdered before being dissolved. Comparatively large volumes of solutions are made in dishes, flasks, or beakers; small quantities in test tubes. As a general rule, it is advisable, when making a solution in a hot liquid, say one of ferrous sulphate (sulphate of iron) in water, to raise the temperature of the liquid to the desired degree before adding the solid to it.

Some solids are readily decomposed when heated. Evidently, solutions of such must be made *in the cold*. Potassium metabisulphite is a good example of such a solid.

2. Crystallisation.—Many substances occur in definite geometrical forms called crystals, these being, to a certain extent, evidence of the definiteness in composition, and, therefore, of the purity of the substance. Crystallisation is usually effected by the evaporation (q.v.) of the liquid, holding the solid in solution until  $(whilst\ hot)$  the solution (q.v.) is saturated. On cooling, crystals will then separate out, since, as a rule, solids are more soluble in hot than in cold liquids. To know when the evaporating hot liquid is saturated, a glass rod is dipped from time to time into it, and the drop on the end of the rod permitted to cool. When this drop crystallises evaporation has proceeded far enough. Another plan is to evaporate the liquid until a pellicle, or skin, forms on its surface.

When it is merely desired to purify a solid by crystallisation, this is dissolved to saturation in the boiling solvent, which is then permitted to cool. The slower the rate of evaporation and of cooling, the larger and finer will the crystals be.

Crystallisation is usually effected in evaporating dishes, which, from their shape, afford a considerable surface for cooling, but ordinary soup plates answer the purpose quite as well.

Crystals are drained and dried on a crystal drainer. Liquids to be crystallised must always be filtered before being set aside, and protected from dust whilst crystallisation is taking place.

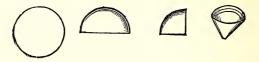
- 3. Evaporation is the conversion of a liquid into vapour, so as to free a dissolved solid from it. The process is carried out, whenever possible, in an evaporating dish, which, on account of the large surface presented by the liquid contained in it, permits evaporation to take place more readily than if a beaker or flask was used. The dish is supported on the ring of a retort stand, or on a tripod, and heated from below by means of a flame of some description.
- 4. Precipitation is, practically, crystallisation effected all at once. Most precipitates are amorphous (non-crystalline), but both precipitation and crystallisation have for object the separation of a solid from a liquid. Precipitation may be chemical or

physical. We have an example of chemical precipitation when we add ammonia to a solution of ferrous sulphate. Here the precipitate is a totally new substance. On mixing a hot saturated solution of ferrous sulphate with three times its volume of alcohol, a precipitate of ferrous sulphate is obtained, owing to the comparative insolubility of this substance in alcohol. A result of this kind is spoken of as physical precipitation.

Precipitation is effected in flasks, or beakers, or on a small scale in test tubes. The colour, appearance, and properties of the precipitates yielded by different substances with various reagents form the basis of qualitative analysis.

5. Filtration is a process used to separate a precipitate from the liquid with which it is mixed, or to free a liquid from suspended dust, &c. We make use for this purpose of a glass funnel, having plugged the apex with cotton-wool; or, more usually, we employ a cone of porous filter-paper, supported in the funnel. If a turbid liquid is poured into a funnel so provided the porous cotton-wool or paper will permit the liquid to pass through whilst retaining the precipitate.

Funnels are themselves supported on the retort stand ring, or on special stands made for the purpose. In most cases, however, it is as convenient to place the funnel in the neck of the flask, etc., in which the filtrate is received.

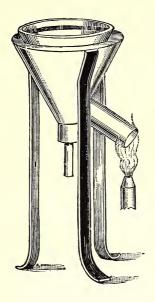


Filter papers are rendered fit for use by being first folded in two and then into a quadrant. On opening this out, so that one fold is at one side and three at the other, a cone is obtained which fits into the funnel. The top of the cones formed by the filtering paper should always be a little below the top of the funnel.

Previous to pouring the liquid into a filter paper, it is best to moisten the paper with distilled water. This reduces to a minimum the chances of the liquid passing through muddy. It sometimes happens that the liquid is so viscous as to pass through the filter with great difficulty, or perhaps not at all. In such cases the following little contrivance will be found very useful. A flask carries a rubber cork pierced with two holes. Through one of these the shank of a funnel passes, and through the other a piece of bent glass tubing. The liquid being poured into the funnel, provided, of course, with a plug of cotton-wool, or with filter paper, the lips are applied to the tube, when, on creating a

partial vacuum by drawing out the air, the viscous liquid will be readily forced through.

Liquids containing gelatine have very often to be filtered, and if the gelatine is hard and present in any quantity the whole liquid is apt to set before filtration can be accomplished.



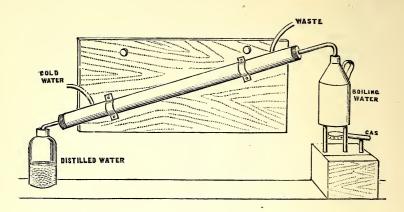
To obviate this the piece of apparatus illustrated is employed. The outer jacket contains water kept hot by a Bunsen burner, and in this the glass funnel fits.

Such an arrangement can be extemporised with a large tin funnel and a small glass one; a rubber cork, or an ordinary one and sealing wax being employed to make a water-tight joint between the two funnel shanks.

6. Distillation is used to separate either a more volatile from a less volatile liquid, e.g., alcohol from water, or to free a liquid, as in making distilled water, from the many substances dissolved in it.

The operation is carried out by placing the liquid to be distilled in a suitable vessel, converting it into vapour, and then condensing the vapour.

A glass Liebig's condenser used with a retort serves for corrosive liquids.

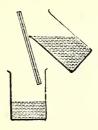


For distilling water and rectifying ether and alcohol the arrangement figured answers every purpose. The condenser proper is made of ordinary tin-plate, the inner tube of solid block tin (not lead). The containing vessel is merely an ordinary tin can connected to the inner tube by corks and glass tubing. The condenser, etc., is fixed to a deal board, which hangs from two nails in the wall.



Many small stills for water only have been brought out from time to time, one of the simplest and most efficient of which is figured herewith. Its use is too self-evident to need detailed description.

- 7. Digestion is a process which has for its object to cause two substances to unite by maintaining them for some time at a more or less elevated temperature. It is evident that one at least of the substances must be a liquid or a solid in solution.
- 8. Decantation is the separation without filtering of a liquid from any sediment or precipitate collected at the bottom of it. In this operation two things are to be guarded against, viz., spilling the liquid and disturbing the precipitate. Usually the



neck of the vessel, presumably a beaker, is greased, and the liquid guided into another vessel by the aid of a previously wetted glass rod, held firmly against the side of the beaker, as shown in the figure. On a larger scale the syphon is employed.

- 9. Pulverisation means reducing a substance to powder, and is always effected in a mortar.
- 10. Washing means the removal of adherent soluble matter from a precipitate, &c. It is effected by directing a stream of water, &c., from a wash bottle over the precipitate supported in a funnel. Evidently, the precipitate must be less soluble than the substances it is desired to eliminate.
- 11. Glass Working.—Tubes and rods are broken by being first scratched with a file and then snapped across. Glass is readily softened by being held for some time in a flame, and this renders it an easy matter to construct bent glass tubes, pipettes, &c. A luminous gas jet, such as that yielded by an ordinary fish-tail burner, makes a more regular bend than a Bunsen or spirit lamp, and should be always employed for that purpose.

To bend a tube it is held in the yellow or luminous portion of the flame, and rotated between the fingers until soft, and then gradually bent, taking care that it is not twisted or pulled whilst bending. If only a Bunsen burner or a spirit lamp are available about an inch of the tube must be kept moving to and fro through the flame, and the bending then carried out as above.

To make a pipette the Bunsen burner is most suitable. In this case the tube is held steadily in the flame until soft, and

the ends are then gradually pushed together until the glass is seen to thicken at the centre, and next suddenly drawn asunder, so as to draw the softened glass out. When cold the thin part is scratched with a file and broken asunder.

Glass rods are made by breaking off the requisite lengths and then rounding the ends by holding them in the flame.

12. Cleaning Apparatus.—Soluble matter is dissolved out with water, boiling if necessary. Insoluble matter, provided it is non-adherent, can be removed with the test tube brush or with a piece of rag tied to the end of a stick. Matters which cannot be thus removed will generally dissolve in boiling nitric acid or in a mixture of nitric and hydrochloric acid.

Grease is got rid of by means of a hot solution of washing soda mixed with some lime.

Methylated spirits or benzene will remove resinous matters. If the latter has been used, the vessel must be rinsed with alcohol to get rid of it.

It is never advisable to dry the *insides* of vessels with a cloth. They should be put away moist and permitted to dry spontaneously. If, however, it is necessary to dry a vessel in a hurry, it can be rinsed first with distilled water, and then with alcohol (pure, not methylated, as this generally contains resinous and other matters), and finally gently warmed.

## QUALITATIVE ANALYSIS.

To test a substance we make use of test tubes, putting into the tube a small quantity of the substance to be tested, or, more usually, its solution, and adding the reagent, which, we suspect, will produce the reaction looked for.

The tubes must, of course, be perfectly clean, and should be washed as soon after use as possible.

A reaction is the characteristic result (production of a precipitate or of an odour, change of colour, &c.) obtained when a reagent acts upon a substance in a way which we know belongs to that substance only.

We may conveniently divide reactions into group reactions and special reactions.

A group reaction is one which occurs with a number of substances, thus enabling them to be grouped together; a special reaction one which is yielded by only one member of a group.

If, for instance, we place in two test tubes equal quantities of our test solutions of silver and lead nitrates, and add to each a drop or two of hydrochloric acid, we shall notice that a white precipitate falls in each case. This is the group reaction of silver and of lead.

But if, having taken fresh portions in clean tubes of our solutions of silver and lead nitrates, we this time add to each some potassium iodide, we shall get with the silver nitrate a

light yellow precipitate, whilst the lead nitrate will give a deep yellow one. Potassium iodide is therefore a special test for either silver or lead.

The metals and inorganic acids admit of being classified in groups, each member of which is characterised by a similar group reaction.

Such a classification of the photographically important metals is made in the following table:—

### THE CHIEF METALS CLASSIFIED INTO GROUPS.

Group Reagent or Reagents.
Group I.—Hydrochloric acid.
Group II.—Hydrochloric acid,
followed by sulphuretted hydrogen.

Group III.—Ammonium chloride, followed by ammonia and ammonium sulphide.

Group IV.—Ammonium chloride, followed by ammonia and by ammonium carbonate. Group V.—No group reagent.

Group Reagent.

same reactions.

Result. White precipitate. Black precipitate.

Yellow precipitate. Whiteish precipitate. Greenish precipitate. Black precipitate. White precipitate. Metal Indicated. Silver, lead. Mercury, copper,

go'd, platinum.
Cadmium.
Aluminium.
Chromium.
Iron.

Magnesium, ammonium, potassium, sodium.

Acid Indicated.

driodic acids.

Acetic, nitric and (occasionally) ni-

Barium, strontium, calcium.

The chief inorganic and some of the organic acids also ad mit being classified into groups, and such a classification is given below:—

### THE CHIEF ACIDS CLASSIFIED INTO GROUPS.

Result.

Group A.—Barium nitrate. White precipitate. Sulphuric, sulphucarbonic, rous, oxalic, phosphoric or boric acids. Group B.-Silver nitrate. Pure white precipitate. Hydrochloric, hydrocyanic, thiosulphuric, hypochlorous or nitrous acids. Dirty white precipitate. Ferrocyanic acid. Reddish brown precipitate. Ferricyanic acid. Black precipitate. Hydrosulphuric acid (occasionally) thiosulphuric acid. Yellowish precipitate. Hydrobromic or hy-

Group C.—No group reagent.

It is almost superfluous to observe with reference to the fore going table that the salts of the acids mentioned will also yield the

Many substances, unfortunately, do not admit of being classified at all, and to detect such we must only rely upon their special reactions. Such reactions will be given in the second part of the work. We will now give such special reactions of the tabulated acids and metals as will enable any one of them to be identified once the group to which it belongs has been discovered.

Group I. (Silver, lead). Silver.—The precipitate given with hydrochloric acid is unsoluble in water, but soluble in ammonia, from which solution it is reprecipitated by an excess of nitric acid. Solutions containing silver give with potassium chromate a brick-red precipitate.

Lead.—The precipitate given with hydrochloric acid is soluble in about 20 times its volume of boiling water, which solution gives a yellow precipitate with potassium chromate. It is also soluble to a certain extent in ammonia, from which solution it is not reprecipitated by an excess of nitric acid.

GROUP II. (Mercury, copper, gold, platinum, cadmium) —The yellow colour of the precipitate at once identifies the cadmium, whilst the blue or green colour of the salt or solution points to the presence of copper. Gold and platinum solutions are generally yellow; mercury solutions colourless. As, however, gold platinum and copper solutions are almost colourless when sufficiently dilute, the following distinctive tests for these metals and for mercury will prove useful.

Copper solutions give with ammonia a light blue precipitate, easily soluble in excess, to a beautiful deep blue liquid. With the same reagent, solutions containing mercury give a white precipitate, and those containing gold or platinum a yellowish one, or else remain unchanged.

Gold solutions boiled with a crystal of ferrous sulphate throw down a brown precipitate of metallic gold, whilst platinum solutions similarly treated suffer no change, unless the boiling is continued for some minutes. As certain salts of platinum (platinous salts) behave like gold in their original condition, the surest plan to discriminate between gold and platinum is to first precipitate with sulphuretted hydrogen, then dissolve the precipitate in the smallest quantity of aqua regia (1 nitric to 3 hydrochloric acid), nearly neutralise the solution with sodium hydroxide, and then add ferrous sulphate, and boil.

Group III. (Aluminium, chromium, iron).—The colours of the respective precipitates here indicate what metal is present.

Group IV. (Barium, strontium, calcium).—Barium salts give a yellow precipitate with potassium chromate. Calcium and strontium salts give no precipitate with this reagent. Strontium salts are precipitated after some time by calcium sulphate, which reagent fails to precipitate calcium solutious.

Group V. (Magnesium, ammonium, potassium, sodium).—Magnesium solutions are precipitated on the addition of ammonium hydroxide, followed by sodium phosphate. The others are not precipitated by these reagents. Ammonium salts evolve the volatile gas ammonia, readily recognised by it familiar smell, when boiled with an excess of sodium hydroxide. Ammonium salts also yield a precipitate when mixed withexcess of tartaric acid solution

Potassium salts act, like ammonium salts, with tartaric acid, but do not, of course, liberate any pungent gas when boiled with sodium hydroxide. The formation of the precipitate which tartaric acid yields with ammonium and potassium is much facilitated by adding sodium acetate to the solution.

Sodium salts are recognised by the intense yellow colour they impart to the non-luminous flame when moistened with hydrochloric acid and held in it, supported on platinum wire.

Group A. (Sulphuric, sulphurous, carbonic, oxalic, phosphoric, boric acids).—The *precipitate* given with barium nitrategives, when mixed with hydrochloric acid, several valuable indications of what acids are present.

If it remains quite unaffected, the acid is sulphuric; if it dissolves with effervescence, the acid is carbonic; if it dissolves without effervescence to a milky liquid, the acid is sulphurous; if it dissolves without effervescence to a clear liquid, the acid is phosphoric, boric, or oxalic. To distinguish between these latter we add silver nitrate to a fresh portion of the original solution, when a yellow precipitate denotes phosphoric and a white one boric or oxalic acids. In the latter case a small portion of the original solid should be boiled in a test tube with sulphuric acid, when effervescence and the escape of a gas easily set fire to at the mouth of the tube denotes oxalic acid.

GROUP B. (Hydrochloric, hydrocyanic, hypochlorous, nitrous, ferrocyanic, ferricyanic, hydrosulphurous, thiosulphurous, hydrobromic, hydriodic, acetic, nitric, and nitrous acids).—The colour of the precipitate sufficiently identifies ferrocyanic and ferricyanic acids.

We may divide the other acids into three sub-groups:—

Black Precipitate.—Smell the original solutions. If odourless, thiosulphuric (hyposulphurous) acid is present. If it smells of rotten eggs the acid is hydrosulphuric.

Yellowish Precipitate.—Mix the original solid with a little manganese peroxide and sulphuric acid and warm. Brown vapours indicate hydrobromic, violet ones hydriodic acid.

White Precipitate.—Boil the liquid with the precipitate at the bottom. If the precipitate blackens, thiosulphuric acid is present. Treat the original solid with one drop of hydrochloric acid. Effervescence and the escape of a gas smelling like almonds indicates hydrocyanic acid. Effervescence and the escape of a gas smelling like seaweed denotes hypochlorous, and effervescence and the escape of a reddish gas, nitrous acid. Warm the original solid with manganese peroxide and sulphuric acid, when the escape of a greenish yellow pungent gas indicates hydrochloric acid.

Group C.—Add some strong sulphuric acid to the original solid. Violent effervescence and the escape of a red gas indicate nitrous acid. If this is not observed, gently warm the mixture, when the evolution of a gas smelling of vinegar denotes acetic acid. If

neither of these are found, add a copper tack to the last mixture and boil it, when the evolution of a red gas denotes nitric acid.

As practice makes perfect, I subjoin a list of substances, all of of them used in photography, small samples of each of which I would recommend my readers to procure and test for themselves, in accordance with the plan I have laid down. In making a solution, put about 30 grains of the substance in a tube and boil it with half-an-ounce of distilled water. This will constitute what I have called the "original solution." If the "original solid" is directed to be used, place half that quantity of the salt in the test tube and add the necessary re-agents to it.

List of Substances for Practice.—Silver nitrate, lead nitrate, mercuric chloride, copper sulphate, gold chloride, chloro-platinic acid (chloride of platinum), potassium chloroplatinite (the Platinotype Company's "platinum salt"), cadmium iodide, common alum, chrome alum, ferrous sulphate (sulphate of iron), barium nitrate, strontium chloride, magnesium sulphate (Epsom salts), calcium chloride, ammonium chloride, sodium chloride, potassium nitrite, sodium sulphite, potassium carbonate, sodium phosphate, sodium acetate, borax, potassium cyanide, calcium hypochloride (bleaching powder), potassium ferrocyanide, potassium ferricyanide, sodium thiosulphate (hypo), potassium sulphide (liver of sulphur), potassium iodide, potassium bromide.

If a clear solution is not obtained by boiling with water, the liquid must be filtered and the filtrate only employed.

# PART II.

### PHOTOGRAPHIC CHEMICALS.

Note.—The substances described are for convenience arranged alphabetically. "Ounces" refers to the ounce of 480 grs., "pounds" to the pound of 12 ounces, and all temperatures are expressed in degrees centigrade.

The following abbreviations are employed throughout:—Syn., synonyms; C., commercial preparation on a large scale; L., laboratory preparation on a small scale; A, appearance, properties, crystalline form, etc.; S., solubility in water and alcohol, or (if a liquid) solvent power; D., distinctive tests; P., purity tests, i.e., tests for impurities; U., photographic uses. The chemical formula is given whenever the substance is a definite chemical compound.

# Acetic Acid.—C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>

Syn., Pyroligneous Acid, Vinegar.

C., two processes are employed on a large scale to obtain this substance - (1) Acetous fermentation, or the oxidation of weak alcohol or liquids containing it. (2) Destructive distillation.

The first process being chiefly employed for the production of vinegar or weak acetic acid, flavoured with certain organic compounds, and intended for dietetic uses, is of no interest to the photographer, so that only the second process will be described.

When wood is heated in closed vessels or destructively distille d a residue of charcoal is left, and the condensed volatile products separate into two layers, the lower of which is wood tar and the upper a mixture of water, methylic alcohol, acetic acid, acetone, and several other substances. To separate these the mixture is first partly re-distilled to get rid of the greater portion of the methylic alcohol, and chalk is added to the residue. By this means the volatile acetic acid is converted into non-volatile calcium acetate, which, on the distillation being now carried to dryness, remains behind, the water and other volatile matters escaping. The impure calcium acetate is next gently heated to decompose any tar which it might contain, and redistilled with sulphuric acid, when crude acetic acid passes over and calcium sulphate remains behind in accordance with the equation Ca  $(C_2H_3O_2)_2 + H_2SO_4 = CaSO_4$ + 2C2H4O2. The crude acid is then neutralised with sodium carbonate, when sodium acetate is formed thus, 2C2H4O2 +  $Na_2CO_3 = 2 NaC_2H_3O_2 + CO_2 + H_2O$ , which is fused to free it from water and from the last traces of tar, and every five parts by weight of it distilled with six parts by weight of pure sulphuric acid, when anhydrous or glacial acetic acid is obtained thus,  $2\text{NaC}_{2}\text{H}_{3}\text{O}_{2} + \text{H}_{2}\text{SO}_{4} = \text{Na}_{2}\text{SO}_{4} + 2\text{C}_{2}\text{H}_{4}\text{O}_{2}$ 

Another process for obtaining glacial acid consists in distilling the crude acid over calcium chloride, which combines with the water present, and prevents it from passing into the distillate.

Some manufacturers employ hydrochloric instead of sulphuric acid. A third process worked on a small scale consists in mixing the crude calcium acetate with a strong solution of calcium chloride, when crystals of calcium aceto-chloride are formed (CH<sub>3</sub>CO<sub>2</sub> CaCl 5H<sub>2</sub>O), from which the acid is got by distillation with sulphuric acid.

The wood employed in the preparation of acetic acid is known as "coppice" wood, being small timber grown for the purpose, and felled when about eighteen years old. Where beech or oak are available, they are highly esteemed. A ton of wood of average quality, and costing 14s., yields 5 cwt. of charcoal, 1½ cwt. of

calcium acetate, and 12 gallons of wood naphtha.

L.—On a small scale glacial acetic acid can be made by neutralising vinegar with sodium carbonate, by adding the latter to it until effervescence ceases, evaporating the liquid to dryness, fusing the residue, and re-distilling it with strong sulphuric acid in the proportions already given, a little manganese peroxide (black oxide of manganese) being added to decompose any sulphurous acid which might be formed.

A.—Pure glacial acetic acid is a colourless liquid, having a rather pleasant characteristic smell, boiling at 118°C., and solidifying at 17°C. It has at 18°C. a spec. grav. of 1.063. The "acetic acid" of the druggist should have a spec. grav. of 1.044, and his "diluted acetic acid" one of 1.006 ("British Pharmacopæia"). The first corresponds to 33 %, the latter to 4.5 % of real acid.

S.—Miscible in all proportions with water and alcohol.

D.—Exactly neutralised with caustic soda, acetic acid forms sodium acetate which can be identified by the usual tests (vide tests

for acetates).

P.—When diluted with six times its volume of water, the solution should give no precipitate with either barium nitrate (sulphwic acid) or with silver nitrate (hydrochloric acid). When the diluted acid is placed in a test tube with a little zinc and hydrochloric acid, the evolved gas should not discolour a strip of paper moistened with lead nitrate (sulphurous acid).

Nitric Acid is detected by adding some fresh solution of ferrous sulphate, followed by strong sulphuric acid cautiously poured down the side of the tube so as not to mix with the acetic acid, when, if nitric acid is present, a brown ring will appear at the junction

of the two liquids.

Formic Acid is detected by boiling with a crystal of silver nitrate,

when a brown colour will be produced.

Furfurol behaves like formic acid with silver nitrate, but is distinguished from it by turning a drop of colourless aniline added to

the acetic acid a deep but transient red.

Acetic acid containing formic acid or furfurol is unfit for use in photography, but such samples can be easily purified by redistilling them, mixed with about 2 % of finely-powdered potassium bichromate, taking care to reject the first ounce or so of the distillate.

The actual strength of a sample of commercial acid can be approximately determined by its solidifying point. To carry out the experiment, about two drachms of the acid is placed in a thin test tube, and the whole cooled by being immersed in powdered hypo, mixed with its own weight of cold water. A thermometer placed in the acid denotes the fall in temperature, and its indication should be taken when the acid is seen to solidify. The following table gives the remaining information:—

Solidifying Points of Acetic Acid of Various Strength.

Solidifying Point.

Percentage of Water.

lidifying Point.	Percentage of
16.5°C.	$\bar{0}$
15.5	.5
15	1
14	1.5
13	2
12	3
10.5	4
10	5
8	7
6	8
5.5	9
4.5	10
4	11
3	12

A far more accurate plan is to determine the specific gravity of the sample, and then make use of the following tables:—

Specific gravity of acetic acid of various strength.

ř	001110 814110		THE TOUR SELECTION	
		Percentage of	_	Percentage of
	Spec. Grav.	Real Acid.	Spec. Gravity.	Real Acid.
	1.002	2.0	1.031	22.0
	1.004	3.0	1.032	23.0
	1.005	4.0	1.033	24.0
	1.007	5.0	1.034	25.0
	1.008	6.0	1.035	26.0
	1.010	7 0	1.036	$27\ 0$
	1.012	8.0	1.038	28.0
	1.013	9.0	1.039	29.0
	1 015	10.0	1.040	30.0
	1.016	11.0	1.041	31.0
	1.017	12.0	1.042	32.0
	1.018	13.0	1.044	33.0
	1.020	14.0	1.051	40.0
	1.022	15.0	1.061	50.0
	1.023	16.0	1.067	60.0
	1.024	17.0	1.070	70.0
	1.025	18.0	1.0735	80.0
	1.026	19.0	1.073	90.0
	1.027	21.0	1.0635	100.0
	1.029	21.0		
	*11 1 1	7 .7 . 71 .7		

It will be observed that a liquid containing 100 per cent. of real acetic acid has the same (1.0635) specific gravity as one containing between 50 and 60 per cent. of real acid.

V.—Acetic acid is employed in photography as a restrainer in acid development, and as a solvent for gelatine in aceto-gelatine emulsions. It fulfils the first part owing to its tendency to form silver acetate with the slowly depositing silver, and the latter owing to its solvent action upon gelatine.

# Acetates, Tests for.

(1.) Mixed with arsenic trioxide, and gently heated, kacodylic exide is given off. (2.) Mixed with sulphuric acid, and gently heated, acetic acid is given off. (3.) Mixed with a little alcohol, and a few drops of strong sulphuric acid, and gently heated, acetic ether is given off. (4) A neutral solution of an acetate gives, with ferric chloride, a red liquid bleached by hydrochloric acid, and becoming turbid and depositing a brown precipitate on boiling. The products liberated by the first three reactions are readily identified by their characteristic odours.

### Albumin.

A substance of indefinite composition, occurring in white of egg and in blood serum, partly as such, and partly in combination as sodium albuminate.

C.—Albumin is obtained from white of egg by beating it up to a froth with water, when the cellules enclosing it burst, and the substance escapes. To remove the broken cellular tissue decantation or filtration is resorted to. In practice the egg-yolks are disposed of to tanners, who utilise them in preparing the finer varieties of leather.

Albumin is obtained from blood serum by permitting the blood to coagulate, and then slicing the clot, when the serum cozes out. Various plans are employed to purify and decolorise this, such as incipient coagulation, filtration through animal charcoal, etc. When purified it is either used at once, or dried at 40°C. When dry it keeps indefinitely, requiring merely to be dissolved in water when about to be used.

L.—Egg and blood albumin contain, in addition to albumin proper and sodium albuminate, considerable quantities of sodium chloride, calcium phosphate, and other extraneous matters. To prepare pure albumin, commercial albumin, in solution, is mixed with lead acetate, when a precipitate of lead albuminate is thrown down. This is repeatedly washed with cold water, and treated, whilst suspended in that liquid, with carbonic acid, when lead carbonate is formed, and albumin remains in solution. The filtrate is then mixed with sulphuretted hydrogen, and heated to 60°C., until it just begins to coagulate, when the first flocks of precipitated albumin carry down with them all the lead as lead sulphide. The solution, which should now be perfectly colourless, is then evaporated to dryness at 40°C.

The following analysis, by Mülder, will show the difference in composition between egg and blood albumin:—

Eg	g Albumir	1.		Blo	od Albumin
~	53.4				53.4
	7.0				7 1
	15.0				15.6
	24.6				22.6
					1.3
		53.4 $7.0$ $15.0$ $24.6$	7.0 15.0	53.4	53.4

Other chemists have found sulphur as an invariable constituent of egg albumin.

A.—Occurs in yellowish shining scales.

S.—Freely soluble in cold water and in strong nitric and acetic acids.

D.—The aqueous solution is coagulated by heat, and gives a white precipitate with dilute nitric or acetic acids, with mercuric chloride, and with silver nitrate. The acetic acid solution gives a precipitate with potassium ferricyanide. Heated in the solid state it swells up, emits a bad odour, and blackens. Heated with a little powdered lime it gives off ammonia, easily recognised by its property of turning blue a piece of moistened red litmus paper placed across the mouth of the tube.

U.—Employed in photography for albuminising paper, in emulsions in conjunction with collodion, and in photo-mechanical processes.

Its use in albuminising paper depends upon the fact that when sodium albuminate, albumin, and silver nitrate are brought in contact, silver albuminate, sodium nitrate, and free nitric acid are formed. The latter, if the solution is sufficiently concentrated, coagulates the albumin, and so keeps the printed image on the surface of the paper; but, to obtain this result, a sufficiently concentrated solution of silver nitrate must be employed, otherwise the albumin will be dissolved. Owing to the fact that silver albuminate reddens on exposure to light, toning is a necessity with such prints. It is used in collodion emulsions for the sake of the greater sensitiveness it confers upon the film, albumin being a much better halogen absorbent than pyroxilin. Its use in photomechanical processes depends upon the fact that it is, like gelatine, rendered insoluble when mixed with potassium bichromate and exposed to light

# Alcohol Ethylic.—C2H5OH.

Syn., Alcohol, Spirits of Wine.

C.—Manufactured by the fermentation of dextrose (grape sugar) or maltose (malt sugar). (1.) The solution containing the dextrose is mixed with yeast and kept at a temperature of about 20°C. for some time, when the yeast converts the dextrose into alcohol and carbon dioxide,  $C_6H_{12}O_6=2C_2H_5OH+2CO_2$ . The product is variously named, according to the source of the sugar. If from grapes it is called brandy, if from molasses, rum, etc. (2.) Starch is by the action of diastase (a nitrogenous substance, occurring

in malted or germinated grain) converted into maltose (or malt sugar) and dextrine, thus:  $3C_6H_{10}O_5 + H_2O = C_{12}H_{22}O_{11} + C_6H_{10}O_5$ , and the maltose can be, like the dextrose, converted into alcohol by yeast, thus:  $C_{12}H_{22}O_{11} + H_2O = 4C_2H_5OH + 4CO_2$  Indian corn, rice, and potatoes are employed to obtain alcohol for manufacturing purposes; barley, rye, and wheat to obtain whiskey.

L.—Any of these mixtures of alcohol with water, &c., will, upon distillation, yield a pure and fairly strong spirit, but the process is not, of course, a very economical one, at least if the whiskey, brandy, etc., have to be purchased to begin with.

To prepare nearly anhydrous alcohol from "rectified" spirit, a pint of the latter is mixed with two ounces of dry and warm potassium carbonate, and the mixture set aside for a couple of days, after which the alcohol is decanted off from the aqueous solution of potassium carbonate, which will have collected at the bottom of the bottle and mixed in a two-pint tin can, with ½lb. of finely powdered, and, if possible, freshly-made quicklime. The can is then tightly corked and set aside for 24 hours, after which it is attached to a condenser, and the liquid distilled until 14 ounces have passed over, the first ounce being rejected. The product should have a spec. grav. of '8 at 15°C.

Alcohol of spec. grav. '815 at 15°C. and quite strong enough for making collodion, can be prepared by mixing a gallon of "rectified" spirit, with two pounds of fused and dry calcium chloride, and distilling after 24 hours' contact, rejecting the first couple of ounces, and collecting seven pints.

Another interesting and fairly efficient method of dehydrating "rectified" spirit consists in filling a clean ox-bladder with it, and suspending the whole in the sun for a few days. In this way alcohol of spec. grav. 9 can be brought down to nearly 8. The action depends upon the fact that animal membranes are pervious to water, but impervious to alcohol. The first three or four lots of spirit strengthened in this way should be redistilled, as they will be contaminated with fatty matters, but after this the bladder can be used without further preparation, and will last a long time.

A.—Perfectly anhydrous alcohol is a colourless liquid, having a characteristic smell and a burning taste, boiling at 78°C., having at 15°C. a sp. gr. of '794, and burning with a pale smokeless flame. Several varieties of it, more or less diluted with water, are met with in commerce. So called "absolute" alcohol contains from 2 to 5%, rectified spirit from 16 to 20%, and proof spirit 51% of water. Rectified spirit is defined by the Pharmacopæia as a liquid containing 84% of alcohol, and having a sp. gr. of '8376 at 15°C. Proof spirit is defined by Act of Parliament as a liquid which "shall at a temperature of 51° Fahr. (105°C.) weigh exactly ½ parts of an equal measure of distilled water." Such a spirit would have a sp. gr. of '92 at 15°C., and contain 49% of alcohol. So many degrees over-proof (O.P.) or under-proof (U.P.) is interpreted as meaning in the former case (O.P.) that 100 gallons

of the O.P. spirit contains as many gallons of pure alcohol as 100 + number of gallons in degrees O.P. of proof spirit. Thus, 10 O.P. means that 100 gallons of such spirit contains as much alcohol as 100 + 10 = 110 gallons of proof spirit. The number of degrees O.P. denotes, in fact, the number of gallons of water requisite to reduce to proof spirit 100 gallons of the spirit in question. So many degrees U.P. denotes the number of gallons of water which would have to be added to 100 less number of degrees U.P. of proof spirit to reduce it to equivalent strength. Thus, 12 U.P. means that 100 gallons of such spirit is equivalent to 100 - 12 = 88 gallons of proof spirit mixed with 12 gallons of water.

As a duty of 10s. is charged on every gallon of proof spirit contained in samples of alcohol unmixed with wood naphtha (vide methylated spirit), such a method of dealing with alcoholic liquids facilitates calculations.

The term "proof spirit" originally denoted alcohol just strong enough to ignite gunpowder when poured over it and then fired,

S.—Alcohol is miscible in all proportions with water and ether. and is a solvent for various gums and resins.

D.—The most characteristic test for alcohol is its property of yielding a precipitate of iodoform when mixed with iodine and potassium hydroxide, thus,  $C_2H_5OH+I_8+6KOH=CH_3I$  (iodoform) +  $CKHO_2$  (potassium formate) + 5KI (potass iodide) +  $5H_2O$ . To carry out the test the liquid to be tested is mixed with a little solid iodine, and then a weak solution of caustic potash is added, until the liquid is nearly, but not quite, discoloured. On stirring with a glass rod, a yellow crystalline precipitate will slowly form on the lines of friction.

P.—The following impurities may be present in commercial samples of alcohol:—

Amylic Alcohol, or fusel-oil; to detect which distil off  ${}^{\Omega}_{0}$ ths of the alcohol at as low a temperature as possible, let the residue cool thoroughly, shake it up with an equal volume of pure petroleum ether, syphon off the upper layer of ether into an evaporating dish, and evaporate to dryness at 80° C., when fusel-oil will be at once detected in the residue by its characteristic and highly unpleasant smell.

Methylic Alcohol, or wood naphtha.—To detect this take 8oz. of the spirit, distil off two ounces of it, dilute the distillate with an equal volume of water, make the liquid strongly alkaline with caustic potash, and add a solution of mercuric chloride drop by drop until the precipitate first formed is just redissolved. Filter the liquid and boil a little of it for a few minutes, when a yellowish, gelatinous precipitate will be produced if methyl alcohol is present.

Acetic Acid is at once detected by the acid reaction of the sample to blue litmus paper.

Aldehyde is detected by adding a little strong solution of silver nitrate, and exposing the whole to light for some hours, when the liquid will gradually blacken if aldehyde is present.

Fixed Impurities are detected by evaporating some of the liquid to dryness at 100°C. in a glass basin.

The quantity of absolute alcohol contained in a commercial sample of spirit can be determined by taking its specific gravity. If, however, other matters besides alcohol and water are present, these must first be removed by distilling  $\frac{T}{8}$  of a measured volume of the spirit and adding sufficient water to make up the original volume.

Specific Gravities of Mixtures of Different Proportions of Alcohol (s.g. 7932) and Water, by Weight, at 17°C. (Meissner).

Parts	s of	Specific Grav.	Part	s of	Specific Grav.	
Alcohol.	Water.	by Weight.	Alcohol.	Water.	by Weight.	
100	0	0.7932	74	26	0.8613	
99	1	0.796	73	27	0.8635	
98	2	0.7988	72	28	0.8657	
97	3	0 8016	71	29	0.868	
96		0.8045	70	30	0.8704	
95	4 5	0.8074	69	31	0 8729	
94	6	0.8104	68	32	0.8755	
93	7	0 8135	67	33	0.8781	
92	8	0.8166	66	34	0.8806	
91	9	0.8196	65	35	0.8831	
90	10	0.8225	64	36	0.8855	
89	11	0.8252	63	37	0.8879	
88	12	0.8279	62	38	0.8902	
87	13	0.8304	61	39	0.8925	
86	14	0.8329	60	40	0.8948	
85	15	0.8353	59	41	0.8971	
84	16	0 8376	58	42	0.8994	
83	17	0.8399	57	43	0.9016	
82	18	0.8422	56	44	0.9038	
81	19	0.8446	55	45	0.9060	
80	20	0.847	54	46	0.9082	
79	21	0 8494	53	47	0.9104	
78	22	0.8519	52	48	0.9127	
77	23	0.8543	51	49	0.915	
76	24	0.8567	50	50	0.9173	
75	25	0.859	49	51	0.9196	

Parts of		Specific Grav.	Par	ts of	Specific Grav.	
Alcohol.	Water.	of Mixture by Weight.	Alcohol.	Water.	of Mixture by Weight.	
48	52	0.9219	23	77	0 9673	
47	53	0.9242	22	78	0 9686	
46	54	0.9264	21	79	0.9699	
45	55	0.928	20	80	0 9712	
44	56	0.9308	19	81	0.9725	
43	57	0.9329	18	82	0.9738	
42	58	0.9350	17	83	0.9751	
41	<b>5</b> 9	0.9371	16	84	0.9763	
40	60	0.9391	15	85	0.9795	
39	61	0.9410	14	86	0.9786	
38	62	0.9429	13	87	0.9796	
37	63	0.9448	12	88	0 9806	
36	64	0 9467	11	. 89	0.9817	
35	65	0.9486	10	90	0.9830	
34	66	0.9505	9	91	0 9844	
33	67	0 9524	8	92	0.9860	
32	68	0.9543	7	93	0.9878	
31	69	0.9561	6	94	0.9897	
30	70	0.9578	5	95	0.9914	
29	71	0.9594	4	96	0.9931	
28	72	0 96 8	4 3	97	0.9948	
27	73	0.9621	2	98	0 9965	
26	74	0.9634	1	99	0.9982	
25	75	0.9647	0	100	1.0000	
24	76	0 966				

V.—Alcohol is employed in photography to manufacture ordinary and enamel collodion, to remove water from gelatine films, so as to enable them to dry rapidly, as a preservative for pyro, and to make varnishes. The first function it fulfils, because, mixed with ether, it dissolves pyroxiline; the second is due to its affinity for moisture; the third to the fact that atmospheric oxygen does not dissolve in it as it does in ordinary water, and the fourth is a consequence of its solvent power upon various gums and resins.

## Alcohol Methylic-CH3OH.

Syn., Wood Spirit, Wood Naptha, Pyroxylic Spirit, Pyroligneous Ether.

C.—Prepared, together with acetic acid (q.v.), by the destructive distillation of wood.

A.—It is met with in commerce as a brown, strongly smelling inflammable liquid, containing, in addition to methylic alcohol (which is colourless and nearly odourless), methylic acetate, acetone, dimethyl-acetal, and a variety of tarry and oily substances.

$\mathbf{The}$	following	table	gives	the	percentage	of	absolute	methyl
alcohol	in wood s	pirit of	differ	ent s	specific grav	itie	s at 15.5°	C.:—

SPE			METHYL ALCOHOL	SPEC. GRAV.	METHYL ALCOHOL
.81	36 97.8	.8822	75.6	•9242	56.8
*82	16 96.1	.8842	73.5	•9266	55.5
.82	56 94	·8876	72 6	•9296	54.2
.83	20 92.3	·8918	71 6	•9344	51.7
.838	34 90.2	.8930	70.3	•9386	49.5
•84	18 889	·8950	69 4	•9414	48
.84	70 863	•8984	68.3	•9448	45.5
.85	85.6	.9008	67.2	•9484	45
.856	84.3	•9032	66.5	•9518	41.5
.859	82.7	•906	65.5	•9540	39.6
.86	12 81.4	.907	64 6	•9564	38
.86	74 80	·9 <b>11</b> 6	63	•9584	36.5
-87	12 78.5	•9154	61.3	•9600	35
.87	12 77 2	•9184	59.6		
.878	34 76.1	•9218	58.2		

It must be remembered that as the composition of crude wood spirit varies considerably the above tables are only approximate.

U.—Employed in a crude state in the manufacture of methylated spirit (q.v.)

# Aluminium Salts, Tests for.

Soluble salts of aluminium give the following reactions:—(1.) Ammonium hydroxide gives a white gelatinous precipitate, insoluble in excess. (2.) Sodium hydroxide gives a white gelatinous precipitate, soluble in excess and reprecipitated by ammonium chloride. (3.) Sodium phosphate gives a white precipitate. (4) Ammonium sulphide gives a dirty white precipitate.

#### Amber.

A fossil resin derived from the *Pinites succinifer*. It contains from 3 to 8 per cent. of succinic acid, a resin soluble in ether, and another soluble in alcohol, besides some other matters.

C.—It occurs as a hard, brittle, yellowish substance, with a resinous lustre, sometimes quite transparent, but ordinarily more or less translucent. The chief supply is derived from the southern shores of the Baltic between Pillau and Grosz-Hubenicken. It is obtained by excavating the ground, but after storms large quantities are thrown up by the waves, evidently derived from veins extending beneath the sea. Pieces are occasionally picked up on the Swedish and Danish coasts, and even on the shores of Norfolk, Essex and Sussex. Minor supplies comes from Basle, Sicily, Northern France, and latterly from Burmah.

L.—Amber for photographic purposes can be purified by being boiled in strong brine for an hour, then well washed, heated in a closed vessel to about 150° C., and lastly, finely powdered with crushed quartz or broken glass.

U.—It is employed in photography to make cold varnish, being dissolved for that purpose in chloroform or benzole.

## Ammonia.—NH3

Syn., Volatile Alkali.

C.L.—Prepared by heating together in a flask an ounce of ammonium chloride with two ounces of calcium oxide, both substances being very finely powdered. On gently warming, ammonia gas is evolved in accordance with the equation  $2NH_4Cl + CaO = CaCl_2 + H_2O + 2NH_3$ . A similar process is adopted on a manufacturing scale.

A.—It is a pungent gas possessing an alkaline reaction. At a temperature of 40°C., or when subjected to a pressure of 61 atmospheres (88lbs to the square inch) at a temperature of 10°C. it condenses to a colourless liquid, which in becoming gaseous, again renders latent or absorbs a large amount of heat. Use is made of this fact to produce artificial refrigeration. For this purpose, two strong vessels, one empty, but in contact with whatever it is desired to cool, the other half filled with the strongest ammonium hydroxide, are connected together. On heating the latter vessel, ammonia gas escapes, and is condensed by its own pressure in the empty receiver. After some time the first vessel is removed from the source of heat and allowed to cool down, when the liquefied ammonia is once more converted into gas and reabsorbed by the water contained in the first vessel, this reabsorption being attended by a very considerable lowering in temperature.

S.—Extremely soluble in water, such a solution being looked upon as ammonium hydroxide (q.v.)

D.—Free ammonia is recognised by (1) its characteristic smell; (2) its effect upon red litmus paper; (3) giving a brown precipitate, or in dilute solutions a brown colour, with Nessler's solution  $(q \ v.)$  (4) giving a white precipitate with solutions of mercuric chlor

U.—Condensed ammonia gas is employed by certain manufacturers of dry plates and of sensitive papers for refrigerating purposes.

# Ammonium Bichromate.—(NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

Syn., Bichromate of Ammonia.

C.L.—Prepared by dividing a solution of chromic anhydride (q.v.) into two portions, neutralising one with ammonium hydroxide, then adding the other, and evaporating to dryness at 100°C. The reaction is  $2\text{CrO}_3 + 2\text{NH}_4\text{OH} = (\text{NH}_4)_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O}$ .

A.—It occurs in powder or in small orange-coloured crystals.

S.—Freely soluble in water.

D.—See Chromates, Tests for, and Ammonium Salts, Test for.

P.—It usually occurs quite pure.

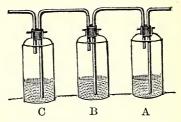
U.—Employed in photography for the same purpose as potassium bichromate (q.v.), over which it has, according to Eder, the advantage of being more than twice as sensitive to light. It is formed in small quantities, when ammonia is added to the potassium bichromate, commonly used for sensitising carbon tissue.

# Ammonium Bromide.—NH<sub>4</sub>Br.

Syn., Bromide of Ammonia.

C.L.—Prepared by (1.) neutralising hydrobromic acid with ammonium hydroxide HBr+NH<sub>4</sub>OH=NH<sub>4</sub>Br+H<sub>2</sub>O.

(2.) Acting on ammonium hydroxide with gaseous bromine  $2NH_3+H_2O+Br_2=2NH_4Br+O$ . The reaction is best brought about by arranging three bottles as shown. A contains liquid



bromine, B strong ammonia, C water. By connecting the outlet of C with an aspirator a mixture of bromine vapour and air is led into B, where most of the ammonium bromide is formed, the water in C retaining any traces which might otherwise escape. A bellows applied to the inlet of A will bring about the same result.

(3.) Acting upon ferrous bromide (q.v.) with ammonium carbonate; thus,  $\text{FeBr}_2 + (\text{NH}_4)_2\text{CO}_3 = 2\text{NH}_4\text{Br} + \text{FeCO}_3$ , insoluble ferrous carbonate being precipitated. About 160 grains of ammonium carbonate will be required for every ounce of bromine taken to make the ferrous bromide.

(4.) Acting upon a solution of potassium bromide with one of ammonium sulphate,  $2KBr + \iota NH_4 \rangle_2SO_4 = K_2SO_4 + 2NH_4Br$ , the comparatively insoluble potassium sulphate being precipitated. To carry out this process 4 ozs. of potassium bromide are dissolved in 6 ozs. of water and mixe 1 with 3 ozs. of ammonium sulphate dissolved in  $4\frac{1}{2}$  czs of water, followed by an ounce of pure alcohol. The whole is then left at rest for 24 hours.

The liquids from (1) and (2) need only to be evaporated at 100°C. to yield ammonium bromide. Those from (3) to (4) must, of course, be first filtered or decanted from the insoluble precipitates.

- A.—Ammonium bromide occurs as a fine, nearly white powder.
- S.—The salt is soluble in  $1\frac{1}{2}$  times its weight of cold water, in 33 times its weight of alcohol of spec. grav. ·8, and is practically insoluble in ether.
  - D.—See Ammonium Salts, Tests for, and Bromide, Tests for.
- P.—It should leave no residue on being heated for some time to redness. If a residue remains, it is probably potassium bromide, and should, after dissolving it in water, be tested for potassium in the usual way.
- U.—Employed as a restrainer in so-called alkaline development, which office it fulfils owing probably to the formation of a double salt with silver bromide more stable than the silver bromide itself. It is also employed in gelatino-bromide emulsion making, as it reacts upon silver nitrate, yielding silver bromide.

Although it was at one time employed in collodion, it has now been to a great extent supplanted by cadmium bromide, which possesses the advantage of being much more soluble in alcoholether.

## Ammonium Carbonate. -(NH<sub>4</sub>)<sub>2</sub> CO<sub>3</sub>

Syn., Carbonate of Ammonia, Sesquicarbonate of Ammonia, Sal Volatile, Preston Salts, Smelling Salts.

Although, for the sake of consistency, the formula for this salt has been represented by  $(\mathrm{NH_4})_2\mathrm{CO_3}$ , the dry commercial salt is really a mixture in variable proportions of the normal carbonate  $(\mathrm{NH_4})_2\mathrm{CO_3}$ , the acid carbonate  $\mathrm{NH_4}\mathrm{HCO_3}$ , and the carbamate  $\mathrm{NH_4}\mathrm{HCO_2}\mathrm{NH_2}$  of ammonium. On treating such a sample with a quantity of water insufficient to dissolve the whole, the acid carbonate remains behind, the normal carbonate is dissolved, and the carbamate is decomposed into the normal carbonate in acordance with the equation  $\mathrm{NH_4}\mathrm{CO_2}\mathrm{NH_2} + \mathrm{H_2O} = (\mathrm{NH_4})_2\mathrm{CO_3}$ , which then passes into solution. A similar change is brought about by dissolving the salt in an excess of water, and then adding ammonia. In this case the acid carbonate is converted into the normal carbonate, thus  $\mathrm{NH_4}\mathrm{HCO_3} + \mathrm{NH_4}\mathrm{OH} = (\mathrm{NH_4})_2\mathrm{CO_3} + \mathrm{H_2O}$ .

C.L.—Made by subliming a mixture of ammonium chloride or sulphate with chalk. (a)  $2NH_4Cl + CaCO_3 = CaCl_2 + (NH_4)_2CO_3$ , a portion of the normal carbonate being decomposed simul-

taneously into acid carbonate and carbamate; (b)  $(NH_4)_2CO_3 = NH_4CO_2NH_4 + H_2O$ ; (c)  $(NH_4)_2CO_5 = NH_4HCO_3 + NH_3$ . A very pure variety occurs as a bye-product in the manufacture of borax from the crude boracic acid of the Tuscan lagoons. This crude boracic acid contains ammonium sulphate, which is converted into carbonate when sodium carbonate is added to the boracic acid to make borax.

A.—Met with in translucent, more or less fibrous masses smelling of ammonia.

S.—Soluble in three times its own weight of water; insoluble in alcohol.

D.—See Ammonium Salts, Tests for, and Carbonates, Tests for.

P.—An aqueous solution of it should give no coloration with ammonium sulphide, and when supersaturated with nitric acid should give no precipitate with either barium nitrate or silver nitrate. The salt itself should volatilise completely on heating.

U.—Employed to prepare ammonium citrate for developing gelatino-chloride plate, and occasionally used to render pyro, etc, alkaline.

#### Ammonium Chloride.-NH4Cl.

Syn., Chloride, Muriate or Hydrochlorate of Ammonia, Sal Ammoniac.

C.—Made on a large scale by mixing "gas liquor" with hydrochloric acid and evaporating to dryness, then washing the tarry salt with a strong solution of pure ammonium chloride, heating it carefully to decompose the tar, and finally subliming it. The "gas liquor" consists of a variety of ammonium salts, most of which are decomposed by the hydrochloric acid. Another and a better process consists in leading the ammonia gas produced by heating gas liquor with lime into hydrochloric acid.

L.—To prepare pure ammonium chloride, finely powdered ammonium sulphate is heated with sulphuric acid until effervescence occurs, and nitric acid is then added in small quantities at a time until the black or brown liquid is discolorised, the whole being finally evaporated down and the ammonium sulphate crystallised out. This is next dissolved in water, lime water added to the solution until the acid is nearly neutralised, the calcium sulphate permitted to subside, and the supernatant liquid heated with excess of slaked lime, the evolved pure ammonia gas being condensed in pure hydrochloric acid, from which solution the ammonium chloride is obtained by evaporation.

A.—It occurs in tough, translucent, fibrous masses, generally coloured brown or yellow by iron. A purer variety is also supplied in small white crystals. Neither varieties smell of ammonia.

S.—Soluble in three times its weight of cold, and in one and a-quarter times its weight of hot water. Sparingly soluble in alcohol.

- D.—See Ammonium Salts, Tests for, and Chlorides, Tests for.
- P.—The salt should completely volatilise on heating, and its solution should not give a precipitate with either barium nitrate (sulphuric acid) or with potassium ferrocyanide (iron).
- U.—Employed in salting albumenised paper, owing to its solubility in water; in preparing a strong solution of mercuric chloride for intensification, owing to its property of causing much more of the mercuric chloride to be dissolved, by converting it into the more soluble double chloride of mercury and ammonium (sal alembroth) HgCl<sub>2</sub>·6NH<sub>4</sub>Cl; and in making gelatino-chloride emulsion for printing out.

#### Ammonium Citrate.

Syn., Citrate of Ammonia.

Three compounds of citric acid and ammonia are known, viz., monammonium citrate  $C_6H_7NH_4O_7$ , diammonium citrate  $C_6H_6$   $(NH_4)_2O_7$ , and triammonium citrate  $C_6H_5(NH_4)_3O_7$ , of which the latter is the one usually employed in photography.

C.L.—Prepared by exactly neutralising citric acid with ammonium hydroxide  $C_6H_8O_7 + 3NH_4OH = C_6H_5(NH_4)_3O_7 + 3H_2O$ .

A.—Occurs as a deliquescent solid.

D.—See Ammonium Salts and Citric Acid.

P.-Usually quite pure.

U.— Employed as a restrainer in the development of gelatino chloride dry-plates.

## Ammonium Hydroxide.—NH40H.

Syn, Ammonium Hydrate, Solution of Ammonia, Liquid Ammonia, Volatile Alkali, Hartshorn.

C.—Prepared from "gas liquor," which contains it, mixed with ammonium sulphide, carbonate, sulphate, chloride, and various other substances. Coal contains nitrogen, and when heated in closed vessels to make illuminating gas some of this passes off as compounds of ammonia (NH<sub>3</sub>) To free the gas from these compounds it is passed through hydraulic mains, i.e., large iron tubes kept partly filled with water, and in which the ammonium salts and the tar condense. The mixture is at intervals allowed to flow into large tanks, where it separates into two layers, the "gas liquor" falling to the bottom and the "gas tar" floating on the top. A ton of coal yields on an average eight gallons of gas liquor, and this yields about 6lbs. of ammonium hydroxide. To obtain the latter from gas liquor it is heated first alone and then with lime, and the evolved ammonia condensed in water. Assuming that ammonium chloride is being decomposed the action is  $2NH_4Cl + CaO = CaCl_2 + 2NH_3 + H_2O$ , and the ammonia gas when passed into water dissolves and becomes ammonium hydroxide, thus  $NH_3 + H_2O = NH_4OH$ .

Much ammonium hydroxide is also made by heating ammonium sulphate or chloride with lime, and passing the gas into water. The water must be artificially cooled to avoid loss, as much heat is evolved during its absorption in water. The following proportions are used in a small manufactory: -61 stone of ammonium chloride and 31 stone of ammonium sulphate are mixed and passed through a sieve. The mixture is then packed in layers with slaked lime in an iron retort, the slaked lime being made by mixing 10 stone of lime with six gallons of water. When the entire mass has been introduced into the retort, 12 gallons of water are added and heat is applied. The gas is first washed by passing it through a quart of water, and then condensed in 30 gallons of icecold water, placed in a vessel surrounded by lumps of ice. After six hours the greater part of the ammonia is condensed in the water. The use of the mixture of sulphate and chloride is to enable the residue to be more readily removed from the retort.

L.—To obtain a chemically pure product, 15 grains of silver nitrate are mixed with 10 ounces of the commercial product, and the mixture gently heated in a retort surrounded by boiling water. The liberated gas is first washed by passing it through an ounce of water, and then condensed in five ounces of ice-cold water. At the expiration of about an hour the operation will be complete. The silver nitrate serves to prevent any traces of ammonium chloride or sulphide from contaminating the distillate, and the low temperature is purposely employed to prevent the volatilisation of any ammonium sulphate.

- A.-Occurs as a colourless liquid, having a characteristic and pungent smell.
- S.—Miscible in all proportions with water and alcohol, and the solution dissolves shellac and many other resinous substances.
- D.—When gently heated, it liberates ammonia gas, which can be identified in the usual way. (See Ammonia.)
- P.—When diluted with four times its own volume of distilled water the liquid should give no precipitate with lime water, denoting absence of carbonic acid; with ammonium oxalate, denoting absence of lime; with ammonium sulphide, denoting absence of copper; and with ammonio-sulphate of copper (made by adding an excess of ammonium hydroxide to a solution of copper sulphate), denoting absence of sulphuretted hydrogen. Another portion supersaturated with nitric acid should give no precipitate with silver nitrate, denoting absence of hydrochloric acid, or with barium nitrate, denoting absence of sulphuric acid. If the solution becomes red when being supersaturated with nitric acid, pyrrol is present.

The actual strength of solution of ammonium hydroxide may be deduced, provided only water is present, from its specific gravity, this decreasing the more ammonia gas the liquid contains. The following table has been compiled for the purpose of valuing commercial ammonia:—

Percentage of Ammonia Gas in Solutions of different Spec. Grav. at 14° Centigrade.

Specific	Percentage	Specific	Percentage	Specific	Percentage	Specific	Percentage
Gravity.	Ammonia.	Gravity.	Ammonia.	Gravity.	Ammonia.	Gravity.	Ammonia.
0·8844	36·0	0·9052	27·0	0.9314	18·0	0.9631	9·0
0 8864	35·0	0·9078	26 0	0.9347	17·0	0.9670	8·0
0·8885	34·0	0 9106	25 0	0.9380	16·0	0.9709	7·0
0·8907	33 0	0·9133	24 0	0.9414	15·0	0.9749	6·0
0·8929	32·0	0·9162	23·0	0.9449	14·0	0.9790	5·0
0·8953	31·0	0 9191	22·0	0.9484	13·0	0.9831	4·0
0·8976	30 0	0·9221	21·0	0.9520	12·0	0.9873	3·0
0·9001	29·0	0·9251	20·0	0.9556	11·0	0.9915	2·0
0·9026	28·0	0·9283	19·0	0.9593	10·0	0.9959	1·0

If other matters are present in any quantity, the specific gravity valuation is of little practical use.

As commonly sold, ammonia hydroxide has a spec. grav. of .89, corresponding to nearly 30 % of ammonia gas (NH<sub>3</sub>). The socalled .88 solution exists only in the imagination of photographic chemists, as it is never made commercially.

U.—Ammonia is used in photography to render pyro, &c., alkaline, and so enhance its deoxidising power, and in gelatinobromide emulsion making by the ammonia process, which latter function it fulfils owing to its property of forming ammonionitrate of silver (AgNO<sub>3</sub>2NH<sub>3</sub>). Ammonia dissolves silver chloride freely, and has for this reason been proposed as a fixing agent for prints on albuminised and other papers. The objections to its use are its pungent smell and the fact that it has only a slight solvent action upon silver-albuminate. It answers quite well, however, to fix prints upon plain salted paper. As solutions of ammonia are more stable the more dilute they are, it is advisable to dilute ammonium hydroxide, when purchased, with a considerable volume of water; and, as it absorbs carbon dioxide from the air, the solution should be kept in a well-stoppered bottle.

# Ammonium Iodide.—NH4I.

Syn., Iodide of Ammonia.

C.L.—Prepared by—(1.) Neutralising hydriodic acid with ammonium hydroxide in accordance with the equation  $\mathrm{NH_4OH} + \mathrm{HI} = \mathrm{NH_4I} + \mathrm{H_2O}$ , and evaporating the solution to dryness, first over a naked flame and finally at  $100^{\circ}$  C. (2) Decomposing a solution of ferrous iodide (q.v.) with one of ammonium carbonate, using half an ounce of the latter for every ounce of iodine originally taken. The mixed solutions are boiled for a short time, the

precipitated ferrous carbonate filtered off, and the filtrate evaporated to dryness. The decomposition is represented thus: FeI<sub>2</sub> + (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> = FeCO<sub>3</sub> + 2NH<sub>4</sub>I. The iodide prepared by either of these processes will be more or less coloured with free iodine; if required perfectly white a little ammonia must be added towards the end of the evaporation. (3.) Decomposing barium iodide (q.v.) with an equivalent quantity of ammonium sulphate, thus,  $BaI_2 + (NH_4)_2SO_4 = 2NH_4I + BaSO_4$ . The barium sulphate is got rid of by filtration, and the filtrate treated as in the second process. (4.) By mixing hot saturated solutions of ammonium sulphate and potassium iodide in equivalent proportions, adding alcohol equal in quantity to 15 % by volume of the water used, letting the whole stand for 24 hours, filtering off the precipitated potasium sulphate, and proceeding as before. The change is represented by  $(NH_4)_2SO_4 + 2KI = K_2SO_4 + 2NH_4I$ . (5.) Acting upon potassium iodide with tartaric acid, and then upon the hydriodic acid formed with ammonium carbonate; thus, (a)  $C_4 H_6 O_6 + KI = HI + C_4 H_5 KO_6$ ; (b) 2HI + $(NH_4)_2CO_3 = 2NH_4I + H_2O + CO_2$ . To carry out this process  $27\frac{1}{2}$  parts by weight of potassium iodide are dissolved in 48 parts by weight of water and mixed with 22 parts by weight of tartaric acid dissolved in 48 parts by weight of water. The mixed sclutions are then placed in pounded ice for half-an-hour, to permit all the potassium hydrotartrate to crystallise out. At the expiration of this time the mixture is filtered and the filtrate treated with ammonium carbonate until effervescence ceases, and finally evaporated to dryness.

A.—Met with in minute yellowish crystals, which should be preserved in the dark in a wel'-stoppered bottle, as the salt is deliquescent, and is decomposed more or less by light. To purify a sample coloured brown by iodine, it may be washed with ether, in which it is practically insoluble, but in which iodine freely dissolves.

S.—Extremely soluble in water, and fairly soluble in alcohol, and in alcohol-ether.

D.—See Ammonium Salts, Tests for, and Iodides, Tests for.

P.—It should leave no residue on being ignited.

U.—It is employed in collodion on account of its solubility in alcohol-ether.

## Ammonium Molybdate.—NH4HM0O4.

Syn., Molybdate of Ammonia.

- C.L.—Prepared by roasting molybdenum glance (MoS<sub>2</sub>), digesting the residue of molybdic anhydride (MoO<sub>3</sub>) with strong ammonia, and evaporating the solution to dryness.
  - A.—Occurs in irregular white opaque crystals.
  - S.—Freely soluble in water.
- U.—Employed as a test for phosphoric acid and the phosphates, with which it gives a yellow precipitate of ammonium phospho-

molybdate. The solution for this purpose is prepared by dissolving an ounce of ammonium molybdate in three ounces of .96 ammonia, and adding to this 12 ounces of nitric acid of spec. grav. 1.2. In carrying out the test, the liquid to be tested must be strongly acidulated with nitric acid, twice its volume of molybdate solution added to it, and the whole finally heated to about 50°C.

# Ammonium Nitrate.—NH<sub>4</sub>NO<sub>3</sub>.

Syn., Nitrate of Ammonia.

- C.L.—Made by neutralising nitric acid with ammonium carbonate; thus  $(\mathrm{NH_4})_2\mathrm{CO}_3 + 2\,\mathrm{BNO}_3 = 2\mathrm{NH_4NO}_3 + \mathrm{H_2O} + \mathrm{CO}_2$ , evaporating to dryness and fusing the residue at a temperature not exceeding 150°C. until steam ceases to be given off. A higher temperature than 150°C. would decompose the salt into nitrous oxide and water.
- A.—It occurs as a semi-crystalline powder, usually more or less deliquesced.
- S.—Soluble in twice its weight of water, the solution being attended by a considerable lowering of temperature.
  - D.- See Ammonium Salta, Tests for, and Nitrates, Tests for.
- U.—A mixture of ammonium nitrate and water has been used in the tropics as a convenient and cheap method of cooling gelatino bromide plates during development to avoid frilling. For this purpose two dishes are used, one within the other, the space be tween the two being packed with ammonium nitrate moistened with water, the inner dish receiving the plate and developer. From the residual solution all the ammonium nitrate can be recovered by evaporation, so that a small supply serves indefinitely.

Ammonium nitrate is always present in baths used with collodion containing ammonium salts, and also in those used to float

albuminised paper salted with ammonium chloride.

# Ammonium Oxalate.—(NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. Sun , Oxalate of Ammonia.

- C.L.—Prepared by neutralising a solution of oxalic acid with one of ammonium carbonate, and evaporating down the liquid thus:  $\frac{H_2C_2O_4 + (NH_4)_2CO_3}{2} = (NH_4)_2C_2O_4 + CO_2 + H_2O$ .
  - A .- It occurs in fine needles, permanent in air.
  - S.—Soluble in twenty times its weight of water.
  - D.—See Ammonium Salts, Tests for, and Oxalates, Tests for.
  - U.—Employed in making ferric ammonium oxalate.

# Ammonium Sulphide. - (NH<sub>4</sub>)<sub>2</sub>S.

Syn., Sulphide or Sulphuret of Ammonia.

C.L.—Prepared by passing sulphuretted hydrogen through ammonium hydroxide until the gas ceases to be absorbed, and then mixing the liquid with a volume of ammonium hydroxide equal to that originally taken, thus (a)  $NH_4OH + H_2S = H_2O + NH_4HS$ ; (b)  $NH_4OH + NH_4HS = (NH_4)_2S + H_2O$ .

A.—A colourless or slightly yellow liquid possessing a most disagreeable smell.

D.—See Ammonium Salts, Tests for, and Sulphedes, Tests for.

U.—Employed in intensification to blacken the mixture of mercurous and silver chloride formed by the action of mercuric chloride upon metallic silver. This it does by converting them both into sulphides, thus  $\mathrm{Hg_2Cl_2} + 2\mathrm{AgCl} + (\mathrm{NH_4})_2\mathrm{S} = \mathrm{Hg_2S} + \mathrm{Ag_2S} + 4\mathrm{NH_4Cl}$ . It is also employed to precipitate silver sulphide from hypo fixing baths in accordance with the equation  $\mathrm{AgNaS_2O_3} + (\mathrm{NH_4})_2\mathrm{S} = \mathrm{Na_2S_2O_3} + (\mathrm{NH_4})_2\mathrm{S_2O_3} + \mathrm{Ag_2S}$ .

It is also largely used in qualitative analysis.

# Ammonium Sulphocyanate.-NH4CnS.

Syn., Sulphocyanide of Ammonia.

C.—Prepared commercially by boiling powdered roll sulphur with the solution of ammonium cyanide, obtained as a bye-

product in the distillation of coal tar.

- L.—A pure product may be prepared by dissolving seven parts by weight of carbon disulphide in thirty parts by weight of absolute alcohol, and gradually adding thirty parts by weight of strong ammonium hydroxide to the mixture, which is then permitted to stand for some days, until it is seen that all the carbon disulphide has been taken up. The change is represented by  $CS_2 + 4NH_4OH = 4H_2O + NH_4CnS + (NH_4)_2S$ . The red solution is finally evaporated down to one-third of its bulk and set aside to crystallise.
  - A.- It occurs in transparent tabular deliquescent crystals.

S.—Soluble in its own weight of water.

- D.—See Ammonium Salts, Tests for, and Sulphocyanates, Tests for.
- U. Employed as a toning agent for gelatino-chloride and other prints in conjunction with sodium carbonate and thiosulphate. It has also been proposed as a substitute for hypo, over which it possesses certain advantages, but it does not appear to have come into general use, probably owing to its relatively high price.

## Ammonium Salts, Tests for.

(1.) Tartaric acid gives in concent ated solutions a white crystal-line precipitate, the formation of which is much promoted by the addition of sodium acetate and by vigorous agitation. (2.) Chloroplatinic acid gives in concentrated solutions a yellow crystalline precipitate, the formation of which is much promoted by the addition of alcohol. (3.) Nessler's solution gives a brown or yellow precipitate or coloration according to the strength of the solution. (4.) On heating with sodium hydroxide, all ammonium salts liberate ammonia gas  $(q \ v.)$ , readily identified by its smell, etc.

# Ammonium Aluminium Sulphate.— $Al_2(NH_4)_2(SO_4)_4$

C.L.—Made like potash alum, substituting ammonium for potassium sulphate. Both this and the potash alum are sold indifferent'y as "alum." Ammonia alum is distinguished from

potash alum by giving off ammonia when warmed with sodium hydroxide.

S.—It dissolves in seven times its weight of cold water.

D.—See Ammonium, Tests for, Aluminium, Tests for, and Sulphates, Tests for.

U.—Same as those of potassium aluminium sulphate (q.v.)

## Anilin.-C6H5NH2

Syn, Phenylamine, Amido-benzene.

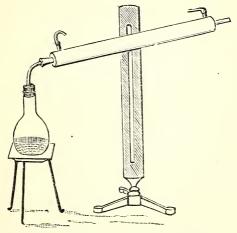
C.—Prepared commercially by placing in an iron retort provided with an agitator and condenser, a mixture of five parts of cast iron filings, eight parts of water, and two parts of strong hydrochloric acid, and adding twenty parts of nitro-benzene with constant stirring. Steam is then blown through the mixture, and more iron filings added until twenty-five parts have been used in all. The reactions may be thus represented:

(a.)  $C_6H_5NO_2 + Fe_3 + 6HCl = C_6H_5NH_2 + 3FeCl_2 + 2H_2O$ .

(b.)  $C_6H_5NO_2 + 6FeCl_2 + 6HCl = C_6H_5NH_2 + 3Fe_2Cl_6 + 2H_2O$ .

An excess of slaked lime is finally added to convert the volatile ferric chloride into non-volatile calcium chloride and ferric hydroxide, and high pressure steam is blown in when water and anilin distil over, the latter sinking to the bottom of the condensed mixture.

L.—On a small scale an ounce of granulated tin is placed in a flask connected with an inverted condenser as shown, and covered



with four fluid ounces of strong hydrochloric acid. Two ounces of nitro-benzene are then added, in small quantities at a time,

through the upper end of the condenser; and when the action has moderated, the mixture is boiled for half an hour and decanted, whilst hot, from the residual tin. On cooling, the liquid will deposit a compound of anilin and tin in fine crystals, which are dried and distilled in a hard glass retort with dry soda lime (a mixture in equivalent proportions of caustic soda and lime), when anilin is set free.

- A.—A yellowish or, when perfectly pure, a colourless liquid having a characteristic ammoniacal-tarry smell.
- S.-Slightly soluble in water, readily soluble in alcohol and in ether.
- D.—Heated with caustic soda and chloroform, the highly offensive and characteristic odour of phenyl-carbamine will be perceived. Bleaching lime gives with an aqueous solution of it a purple-violet co'our, rapidly changing to brown.
- U.—Employed in the manufacture of cyanin. By acting upon anilin with caustic soda and methyl chloride, methylanilin is obtained, used in the manufacture of methyl orange.

## Antimony Sulphide.—Sb<sub>2</sub>S<sub>3</sub>

Syn., Antimonious Sulphide, Sulphide of Antimony, Stibnite, Grey Antimony Ore.

Occurs naturally as a heavy mineral of a dark grey colour in

Cornwall, Hungary and Borneo.

- C.—To purify the mineral, it is gently heated on the sloping hearth of a reverberatory furnace, when, by the process known as liquation, antimony sulphide melts and flows away, leaving the earthy matters behind. The product thus obtained is known as crude antimony, and this, when powdered, constitutes the sulphide sold commercially.
  - A. A black powder resembling plumbago.
- D.—Heated with hydrochloric acid it liberates sulphuretted hydrogen recognisable by its smell, and the solution poured into water deposits an orange precipitate.
- U.—Employed to make flash mixtures for photography at night by being mixed with sulphur, potassium chlorate, and magnesium powder.

## Aqua Regia.

- C.L.—Made by mixing four volumes of concentrated hydrochloric acid with one volume of concentrated nitric acid.
- A.—A yellowish liquid, which liberates yellow fumes when gently warmed.
- U.—Employed for the purpose of dissolving gold and platinum, to which former property its name is due, gold being considered the "king" of metals. It acts upon these metals in virtue of the free chlorine it contains, the action of nitric and of sulphuric acid upon each other being represented by HNO<sub>3</sub> + 3HCl = NOCl + Cl<sub>2</sub> + 2H<sub>2</sub>O.

## Aurine.-C<sub>19</sub>H<sub>14</sub>O<sub>3</sub>

C.—Prepared commercially by heating a mixture of phenol (carbolic acid), oxalic acid, and sulphuric acid, when a crude product is obtained.

This is dissolved in warm ammonium hydroxide, and the liquid permitted to cool, when a crystalline precipitate falls, which is purified by being washed with alcohol. The ammonia compound so obtained is then decomposed by acetic acid, when aurin is set free, and can be further purified by re-crystallisation from glacial acetic acid.

- L.—On a small scale it may be prepared by heating dry phenol with caustic soda and mercuric oxide, or by boiling magenta (rosanilin acetate) with potassium nitrate.
- A.—A dark-coloured gum-like substance with a reddish green lustre.
  - S.—Insoluble in water; freely soluble in alcohol and ether.
- U.—Used for dyeing fabrics for dark-room windows, and mixed with collodion as a backing for dry plates, both of which purposes it serves on account of its highly non-actinic colour.

Note — Methyl aurin, rosaurin, or rosolic acid, C<sub>20</sub>H<sub>16</sub>O<sub>3</sub>, is frequently sold as aurin, and possesses similar properties.

#### Azaline.

The trade term for a mixture of quinolin red and cyanin blue, used in orthochromatic work. The name is also applied to a nitrate of rosanilin sold as rubine, new red and fuchsine.

- C.L.—The solution usually employed in orthochromatic work is made by dissolving 15 grs. quinoline red and  $1\frac{1}{2}$  grs. cyanin blue in 20 oz. of alcohol.
- D.—The alcoholic solution is an intensely carmine liquid with vivid reddish-brown fluorescence. Hydrochloric acid changes it to yellowish red, and ammonia, added to this solution, restores its original colour. Diluted freely and exposed to light the same change is brought about.

## Barium Bromide.—BaBr<sub>2</sub>2H<sub>2</sub>O.

Syn., Bromide of Barium or of Baryta.

- C.L.—Made by neutralising hydrobromic acid with barium carbonate  $2 \mathrm{HBr} + \mathrm{BaCO}_3 = \mathrm{H_2O} + \mathrm{CO}_2 + \mathrm{BaBr}_2$ , or by the same process as that used in making calcium bromide (q.v.), substituting barium hydroxide for milk of lime.
  - A.—Occurs in white tabular crystals.
  - S.—Freely soluble in water and alcohol.
  - D.—See Barium Salts, Tests for, and Bromides, Tests for.
  - U .- Sometimes emp'oyed in collodion.

## Barium Carbonate.—BaCO<sub>3</sub>

Syn., Carbonate of Barium or of Baryta. Occurs native as

C L.—Prepared artificially from heavy spar or barium sulphate by mixing 50 parts of the finely pulverised mineral with 100 parts of dry sodium carbonate, 600 parts of powdered nitre, and 100 parts of powdered charcoal. The mixture is then placed on an iron plate and kindled, when it burns and leaves a residue of sodium sulphate and barium carbonate. The reaction really takes place between the barium sulphate and sodium carbonate, thus  ${\rm BaSO_4} + {\rm Na_2CO_3} = {\rm Na_2SO_4} + {\rm BaCO_3}$ , the charcoal being used as fuel, and the nitre as a source of oxygen to make it burn readily. On boiling the fused residue with water, the sodium sulphate dissolves, and the barium carbonate remains behind. This should be then washed until the washings cease to give a precipitate with barium nitrate.

- A.—A white amorphous powder.
- S.—Insoluble in water or alcohol.
- D.—See Barium Salts, Tests for, and Carbonates, Tests for.
- U.- The chief source of other barium compounds.

## Barium Iodide.-Bal,

Syn., Iodide of Barium or of Baryta.

C.L.—Made by warming together for some time a mixture of iron filings (in excess) with water and iodine, and adding barium hydroxide solution to the filtrate as long as a precipitate continues to fall. On filtration and evaporation barium iodide crystallises out, thus  $Fe+I_2=FeI_2$ , and  $Ba(OH)_2+FeI_2=Fe(OH)_2+BaI_2$ .

Another process consists in mixing one part of amorphous phosphorus with 40 parts of warm water and 24 parts of finely-powdered iodine, when hydriodic acid and phosphorus acid are formed, thus  $P+5I+4H_2O=5HI+H_3PO_4$ . The liquid, which should be quite colourless, is then treated with barium carbonate until effervescence ceases, and barium hydroxide in solution is then added to slightly alkaline reaction. The following equation represents the change:  $-10HI+2H_3PO_4+8BaCO_3=5BaI_2+Ba_3(PO_4)_2+8CO_2+8H_2O$ . The insoluble barium phosphate is then filtered off a current of carbon dioxide passed through the liquid to decompose any residual barium hydroxide, and the filtrate finally evaporated down.

- A.—Occurs in deliquescent tabular crystals.
- S.—Soluble in water, almost insoluble in alcohol, slightly soluble in ether.
  - D.—See Barium Salts, Tests for, and Iodides, Tests for.
  - U .- Employed in collodion.

## Barium Chloride.—BaCl<sub>2</sub> + 2H<sub>2</sub>O.

Sym, Chloride of Barium or of Baryta.

- C.—Made on a large scale by strongly heating in a reverberatory furnace a mixture of powdered heavy spar (BaSO<sub>4</sub>) with calcium chloride, chalk and coal dust, and extracting the residue with water. The change may be looked upon as occurring in three stages, viz.:—
  - (a.)  $BaSO_4 + 4C = BaS + 4CO$
  - (b.)  $BaS + CaCO_3 = BaCO_3 + CaS$
  - (c.)  $BaCO_3 + CaCl_2 = BaCl_2 + CaCO_3$

the soluble barium chloride being finally dissolved out by the water.

- L.—A pure product can be prepared by neutralising hydrochloric acid with barium carbonate, thus  $2HCl + BaCO_3 = BaCl_2 + H_2O + CO_2$ , and crystallising out the barium chloride.
  - A .- It occurs in white, permanent tabular crystals.
- S.—Soluble in twice its weight of cold water; insoluble in alcohol.
  - D.—See Barium Salts, Tests for, and Chlorides, Tests for.
- U.—Occasionally employed as a substitute for sodium or ammonium chloride in salting albuminised paper.

## Barium Hydroxide. $-Ba(OH)_2 + 8H_2O$ .

Syn., Hydrate of Barium, Hydrate of Baryta, Caustic Baryta, Baryta.

- C.L.—Made by adding four parts of powdered barium nitrate to a boiling solution of sodium hydroxide, prepared by dissolving three parts of that substance in twenty parts of water. The mixture is boiled for ten minutes, filtered, permitted to stand for ten minutes more, decanted off from the excess of barium nitrate which has separated out, and finally allowed to get quite cold, when crystals of barium hydroxide will separate out, the more soluble sodium nitrate remaining in solution. The crystals should be rapidly dried and preserved in a well-stoppered bottle. The following equation represents the change:—Ba(NO<sub>3</sub>)<sub>2</sub> + 2NaOH = 2NaNO<sub>3</sub> + Ba(OH)<sub>2</sub>.
  - A.—Occurs in whitish ill-defined crystals.
- S.—Soluble in water, yielding a more or less turbid solution; insoluble in alcohol.
  - D.—Gives a dense white precipitate with dilute sulphuric acid.
  - U.—Employed to prepare barium iodide, etc.

## Barium Nitrate. - Ba(NO3)2

Syn., Nitrate of Barium or of Baryta.

C.—Prepared commercially by dissolving native barium carbonate (witherite) in nitric acid.

- L.- On a small scale the same process may be adopted, using the precipitated carbonate instead of the naturally occurring product. When the acid is neutralised the solution may be evaporated down and the salt crystallised out. The following equation represents the change:— $BaCO_3 + 2HNO_3 = Ba(NO_3)_2 + CO_2 + H_3O$ .
  - A.—Occurs in octahedral, translucent crystals.
- S.—Soluble in twelve times its weight of cold water; insoluble in alcohol.
  - D.—See Barium Salts, Tests for, and Chlorides, Tests for.
- U.—Employed in photography to make ferrous nitrate solution, used as a wet plate developer, by mixing it with a solution of ferrous sulphate, and permitting the precipitate of barium sulphate to subside, thus  $\text{Ba}(\text{NO}_3)_2 + \text{FeSO}_4 7\text{H}_2\text{O} = \text{BaSO}_4 + \text{Fe}(\text{NO}_3)_2 + 7\text{H}_2\text{O}$ . It is also recommended as an addition to the silver bath used in the collodion process, as it prevents pinholes by decreasing the solvent action of silver nitrate upon siver iodide. A solution of it is employed as a test for sulphuric acid and the sulphates.

## Barium Salts, Tests for.

Soluble barium salts are characterised by the following reactions.

- (1)—Calcium sulphates gives an immediate white precipitate.
- (2).—Sulphuric acid gives a white precipitate.
- (3.)—Potassium chromate gives a yellow precipitate.
- (4.)—Ammonium carbonate preceded by ammonium hydroxide and chloride gives a white precipitate.

## Benzene.-C6H6

Syn, Benzole.

- C.—Obtained commercially as one of the products of the distillation of the "light oil" got from coal tar.
- A.—A colourless, mobile, volatile liquid, smelling like coal gas.
- S.—Insoluble in water, miscible with ether and alcohol. It dissolves wax, amber, and other kindred substances.
  - D.—Sufficiently identified by its appearance and smell.
- P.—Liable to contain a little water, but can be dehydra'ed by redistilling it over dry plaster of Paris.
- U.—Employed in photography to make encaustic paste and cold varnish, the former a solution of white wax, and the latter a solution of amber in it. It is also used in the manufacture of nitro-benzene and diazobenzene sulphonic acid (q.v)

#### Bitumen.

Syn., Asphaltum, Pitch.

A substance of indefinite composition, usually containing carbon, hydrogen and oxygen, with, in some cases, a small proportion of nitrogen. Some samples contain no oxygen, and sulphur is present in others. It occurs naturally on the shores of the Dead Sea (whence its name "Jew's" pitch or bitumen of Judæa), and in Syria, Trinidad, Coxitambo, Peru, and Cuba. Inferior varieties are also met with in several parts of Europe.

A.—It occurs commercially in black or brown lumps, having a shiny conchoidal fracture, and a slight tarry smell.

L. — To "prepare" bitumen for photographic purposes, the following processes are made use of : -(1). The commercial product is finely powdered and digested with alcohol for a couple of hours in a closed vessel at a temperature of 40°C., after which the residue is collected on a filter, washed with alcohol, and left for several days in contact with an excess of ether. The residue is finally airdried and preserved in the dark. (2.) Powdered Syrian bitumen is treated with twice its weight of turpentine, and this solution is then shaken up with ether, which dissolves out the most sensitive portion, and on careful distillation to recover the ether, leaves it behind in the flask or retort. The treatment with alcohol in the first process separates the bitumen into three portions, the first soluble in alcohol, the second soluble with ether, and the third insoluble in both. The fraction soluble in alcohol is black and hard, and has an interest smell of tar; that soluble in ether is brown and soft, and almost inodorous, and that insoluble in both is black and quite inodorous. The latter fraction is by far the most sensitive to light.

Syrian bitumen contair s 52 %, Trinidad only 38 % of the portion most sensitive to light, hence the former is preferred for photographic purposes. An ultimate analysis of the two chief varieties is appended—

	S	Syrian	$\mathbf{r}$	Trinidad		
Carbon	 	80.0			78.8	
Hydrogen	 	6.0			9.3	
Sulphur	 	10.0			10.0	
Nitrogen	 	6			•5	
Ash	 	•4		• •	14	
		100.0			100.0	

- S.—Insoluble in water, partly soluble in alcohol and ether, almost completely soluble in benzole, chloroform, carbon, disulphide, turpentine, and oil of lavender. The "prepared" variety is completely soluble in turpentine and in chloroform.
  - D.—Sufficiently identified by its appearance.
- P.—Sometimes adulterated with coal-tar pitch; a fraud detectable by breaking the sample, when it will be seen to possess a dull instead of a shining fracture, or by melting it at as low a

temperature as possible, when it will be found impossible to draw it into threads, and it will be seen to possess a granular uneven appearance when broken across whilst hot.

U.—Owing to the fact that the action of light renders bitumen, especially when "prepared," insoluble in its usual solvent, this substance is employed extensively in many photo-mechanical processes. It has the great advantage over bichromated albumen or gelatine of being unacted upon by nitric acid. The action of light is probably physical, and not chemical, as it has been found that insolated and insoluble bitumen has its solubility restored by merely remelting it.

## Bleaching Lime.

Syn., Chloride of Lime, Chlorinated Lime, Bleaching Powder,
Hypochlorite of Lime.

C.L.—Made by passing chlorine gas over slaked lime, when the following reaction occurs:  $-2\text{Cl}_2+3\text{Ca}(\text{OH})_2=\text{CaCl}_2+2\text{CaOClOH}+2\text{H}_2\text{O}$ . On treating it with water the calcium chloride (CaCl<sub>2</sub>) dissolves, and the calcium hydroxychloride (CaOClOH) decomposes into calcium hydroxide (CaO<sub>2</sub>H<sub>2</sub>), which remains undissolved, and calcium hypochlorite (CaCl<sub>2</sub>O<sub>2</sub>), which passes into solution. The latter change is represented by  $2\text{CaOClOH} = \text{CaCl}_2\text{O}_2 + \text{Ca} \text{CaCl$ 

A.—Occurs as a dirty-white soft powder, often agglomerated into small lumps, and having a peculiar chlorous smell. Upon exposure to air it deliquesces more or less.

S.—Decomposed by water, the calcium hypochlorite formed then entering into solution; insoluble in alcohol.

D.—See Calcium Salts, Tests for, and Hypochlorites, Tests for.

U.—Employed in photography, mixed with gold chloride, for toning paper prints. Assuming the product of the insolation of silver chloride to be silver oxychloride, the following equation would represent the change:  $-\text{CaCl}_2\text{O}_2 + 2\text{AuCl}_3 + \text{Ag}_2\text{O} \cdot 2\text{AgCl} + 3\text{H}_2\text{O} = \text{Ca}(\text{ClO}_3)_2 + 6\text{HCl} + \text{Au}_2 + \text{Ag}_2 + 2\text{AgCl}$ , the calcium hypochlorite becoming converted into calcium chlorate, and the image becoming covered with metallic gold.

## Borates, Tests for.

Soluble borates give the following reactions:—(1.) Mixed in an evaporating dish with a little sulphuric acid and some alcohol, a green colour is imparted to the otherwise colourless flame obtained when the alcohol is kindled. (2.) Barium nitrate gives a white precipitate, soluble without effervescence in hydrochloric acid. (3.) Silver nitrate gives a dirty-white precipitate, provided the solution is sufficiently concentrated. (4.) Sulphuric acid, added to a concentrated solution, gives on cooling a crystalline precipitate.

#### Bromine.—Br.

C.—Most of the bromine met with in commerce is obtained from the salt springs of Stassfurt. The liquid is first concentrated by evaporation, and the less soluble salts removed. A current of chlorine is then passed into the liquid, when the bromine, which is present chiefly as magnesium, sodium and dotassium bromide, is liberated in the free state, potassium chloride being formed thus, KBr + Cl = KCl + Br. The orange-coloured liquid so obtained is shaken up with ether, which dissolves out the bromine, and the ethercal solution of bromine is next mixed with sodium hydroxide, by which the volatile bromine is converted into non-volatile sodium bromide and bromate, in accordance with the equation  $6\text{NaOH} + 6\text{Br} = 5\text{NaBr} + \text{NaBrO}_3 + 3\text{H}_2\text{O}$ . The greater part of the ether now freed from bromine is syphoned off and the remainder recovered by distillation, the residue of sodium bromide and bromate being strongly heated to decompose the bromate into bromide thus, NaBrO<sub>3</sub>=NaBr+O<sub>3</sub>. The sodium bromide so obtained is finally distilled with manganese peroxide and sulphuric acid, when bromine is liberated and condensed in well-cooled receivers,  $2\text{NaBr} + \text{MnO}_2 + 2\text{H}_2\text{SO}_4 = \text{KNa}_2\text{SO}_4 + \text{MnSO}_4 +$  $2H_{2}O + Br_{2}$ .

A portion of the bromine met with in commerce is obtained as a bye-product in the manufacture of iodine (q.v.), but these samples are almost invariably contaminated with traces of the latter element.

Owing to the difficulty of transporting such a dangerous liquid as bromine, that manufactured from Stassfurt salts is first converted into ferrous-bromide, and exported as such. A concentrated solution of the latter can be readily decomposed as required by passing chlorine through it thus,  $\text{FeBr}_2 + \text{Cl}_2 = \text{FeCl}_2 + \text{Br}_2$ .

L.—To purify commercial bromine it is saturated with barium hydrate, the solution evaporated, and the residue ignited, and treated with strong alcohol, in which barium bromide only is soluble. On distilling to recover the alcohol pure barium bromide is got, and from this pure bromine can be prepared in the usual way.

A.—It occurs as a very volatile dark brownish-red heavy liquid, with a most unpleasant and characteristic smell. Bromine itself and its vapour are highly poisonous. Owing to its volatile nature,

it is best preserved under water in a well-stoppered bottle.

S.—Soluble in water, alcohol, and ether.

D.—Sufficiently characterised by its appearance and smell.

P.—To detect iodine in bromine, mix it with caustic soda until distinctly alkaline, and add a little starch paste to the mixture. If now a trace of chlorine water be dropped in, the characteristic blue colour of starch and iodine will be developed. To detect chlorine, completely precipitate an aqueous solution of the sample with silver nitrate, and digest the well-washed precipitate with 10% ammonium hydroxide. If any chlorine is present, the filtrate will become turbid on supersaturating it with nitric acid.

U.—Bromine water has been proposed, followed by hypo, to reduce gelatino-bromide prints. The action depends upon the fact that the bromine acts the silver of the image, forming silver bromide, which in its turn is dissolved by the hypo. It has also been advocated as a hypo eliminator, as when bromine and sodium thiosulphate are mixed, sodium tetrathionate and sodium bromide are formed thus,  $2Na_2S_2O_3+Br_2=Na_2S_4O_6+2NaBr$ .

# Bromides, Tests for.

The soluble bromides are distinguished by the following reactions:—(1.) Heated in the solid state with strong sulphuric acid and manganese peroxide they liberate brownish red vapours of bromine (2.) Their solutions give with silver nitrate a yellowish white precipitate slightly soluble in strong ammonia, but insoluble in a weaker solution. (3) Chlorine water added to a bromide decomposes it, liberating bromine, and forming a chloride; a little ether shaken up with such a solution will dissolve the bromine and float at the top as a brown or yellow layer. (4.) Lead nitrate gives a white precipitate soluble in boiling water.

To detect a bromide in presence of an iodide or chloride, add some dilute sulphuric acid to the solution, then starch paste, and finally a few drops of fuming nitric acid. Now gradually drop in chlorine water until the blue colour given with the starch paste is destroyed, and continue adding the chlorine water until it is present in slight excess. Finally shake up with chloroform, which will dissolve any bromine present, and form with it a yellow or brown layer at the bottom of the liquid.

#### Cadmium.—Cd.

- Q.—Occurs naturally as cadmium sulphide in certain zinc cres, and in the preparation of zinc from these by distillation with coal dust, the cadmium, being more volatile than the z nc, is found in the first portions of the distillate. This is dissolved in sulphuric acid, and sulphuretted hydrogen passed through the solution, when the cadmium separates out as yellow cadmium sulphide (CdS), used as a yellow paint under the name of cadmia. To prepare the metal, this cadmia is dissolved in hydrochloric acid, and ammonium carbonate added to the solution, when cadmium carbonate is precipitated, and this mixed with charcoal powder and distilled yields metallic cadmium.
- A.—A malleable, ductile, white metal, marking paper like lead, and emitting when bent a "cry" like tin. Cadmium salts are poisonous, the antidotes being sodium carbonate and white of egg.
- D.—Readily soluble in hydrochloric acid, which solution gives a yellow precipitate with sulphuretted hydrogen.
- P.—The hydrochloric acid solution supersaturated with sulphuretted hydrogen and filtered should give no precipitate when neutralised with ammonium hydroxide and treated with potassium ferrocyanide. If a precipitate falls zinc is present.

## Cadmium Bromide.— $CdBr_2 + 4H_2O$ .

Syn., Bromide of Cadmium.

- C.L.—Made by digesting an excess of cadmium filings with hydrobromic acid or a mixture of bromine and water, filtering and evaporating.
- A.—Occurs in small white somewhat efflorescent needles. Heated to 150° C, the four molecules of water of crystallisation are driven off and the salt is rendered anhydrous.
  - S.—Readily soluble in water and alcohol.
  - D.—See Cadmium Salts and Bromides.
- P.—The slightly acidified solution supersaturated with sulphuretted hydrogen and filtered should give no precipitate with potassium ferrocyanide.
- U.—Employed in collodion, owing to its solubility in alcohol ether, and the great permanence of such solutions.

## Cadmium Iodide.—CdI<sub>2</sub>

Syn., Iodide of Cadmium.

- C.L.—Made like cadmium bromide, using hydriodic acid or iodine and water.
  - A.—Occurs in pearly, nearly white plates.
- S.—Soluble in its own weight of water and in alcohol and in ether.
  - D.-See Cadmium Salts and Bromides.
  - P.U.—Same as cadmium bromide.

## Cadmium Salts, Tests for.

Soluble cadmium salts are distinguished by the following reactions:—(1.) They give with sulphuretted hydrogen in faintly acid, neutral, or alkaline solutions a yellow precipitate, insoluble in caustic soda. (2.) They give a white precipitate with ammonium or sodium hydroxide, the precipitate yielded by the former insoluble, that yielded by the latter freely soluble in an excess of the precipitant.

#### Calcium Oxide.-CaO.

Syn., Lime, Quicklime, Caustic Lime.

- C.L.—Made by exposing chalk, marble, limestone, or any variety of calcium carbonate to a red heat, the decomposition being effected on a large scale in a limekiln. Conveniently made on a small scale by calcining egg-shells in a clear fire or over a Bunsen burner. The change is represented thus, CaCO<sub>3</sub> = CaO + CO<sub>2</sub>.
- A.—Occurs in white (if pure) lumps, which, when moistened with water, swell up, become hot, and crumble to powder, owing to the formation of calcium hydroxide,  $CaO + H_2O = Ca(OH)_2$ .

- S.—Very slightly soluble in water, insoluble in alcohol. The addition of sugar-candy in the proportion of two parts of sugar to one of lime enables water to take up a much larger quantity of the latter.
  - D.—See Calcium Salts.

U.—Plain lime water is employed as a test for a variety of substances, and the solution of it with sugar is available for rendering pyro, etc., alkaline, blackening negatives whitened with mercury, etc.

# Calcium Bromide.—CaBr<sub>2</sub>+4H<sub>2</sub>O.

Syn., Bromide of Calcium.

C.L.—Prepared on a large scale for use in the manufacture of other bromides in the following way: 20 parts of flowers of sulphur are addd to 60 parts of liquid bromine, when combination quietly occurs, bromine disulphide (Br<sub>2</sub>S<sub>2</sub>) being formed, mixed with an excess of bromine. The liquid is then slowly poured over milk of lime (obtained by mixing slaked lime with five times its weight of water), when calcium bromide, sulphate and hydroxysulphide are formed. By treating the residue with a little water, the bromide is all dissolved out together with traces of the other compounds. To decompose these the liquid is boiled with a few drops of sulphuric acid, filtered, made alkaline with lime water, reduced to one-third of its bulk by evaporation, and permitted to stand for some time, when the last traces of calcium sulphate separate out. The decanted liquid is then evaporated to dryness at 100°C.

- A.—Occurs as a deliquescent white powder.
- S .- Freely soluble in water and in alcohol.
- D.—See Calcium Salts and Bromides.
- U.—Employed to make other bromides.

## Calcium Hydroxide.—Ca(OH)2

Syn., Calcium Hydrate, Hydrate of Lime, Slaked Lime.

C.L.—Prepared by moistening quicklime with about five times its weight of water,  $CaO + H_2O = Ca(OH)_2$ .

- A.-A soft white powder.
- S.—Soluble in 700 times its weight in water, the solution constituting the so-called lime water.
  - D.-See Calcium Salts.
  - U.-Employed to render certain toning baths alkaline.

# Calcium Chloride. $-\text{CaCl}_2 + 2\text{H}_2\text{O}$ .

Syn., Muriate of Lime, Chloride of Calcium.

C.—Occurs as a bye-product in the manufacture of ammonium hydroxide.

L.—On a small scale a pure product may be obtained by dissolving precipitated chalk or Iceland spar in hydrochloric acid,  $CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$ , evaporating to dryness.

- A.—Occurs in porous, deliquescent masses.
- S.—Soluble in twice its weight of water, insoluble in alcohol.
- D .- See Calcium Salts and Chlorides.
- P.—Commercial samples usually contain iron, detected by the blue precipitate which their solutions yield with potassium ferrocyanide.
- U.—In the crude state it is employed as a drying agent in the platinotype process; in the pure condition in certain emulsion processes.

## Calcium Carbonate.—CaCO3

Syn., Carbonate of Lime or of Calcium.

Occurs native as limestone, chalk, marble, calc spar, arrogonite, satin spar, and Iceland spar, the latter being perfectly pure, and white marble almost pure. It is also the chief constituent of egg-shells and of oyster and lobster shells, etc. Coral has practically a similar composition.

- C.L.—Manufactured as "prepared chalk" by mixing finely-powdered chalk with water, letting the mixture settle for a short time, and pouring off the milky liquid into another vessel, at the bottom of which it deposits, after some hours, a fine precipitate of calcium carbonate. It is also manufactured as "whiting" by grinding chalk to a paste with water and drying the mixture. "Precipated chalk" is prepared by mixing solutions of calcium chloride and sodium carbonate, and well washing the precipitate, CaCl<sub>2</sub>+Na<sub>2</sub>CO<sub>3</sub>=2NaCl+CaCO<sub>3</sub>.
- A.—Iceland spar occurs in transparent rhombic crystals, prepared chalk as a white powder.
- S.—Insoluble in alcohol and in pure water, soluble to a slight extent in water containing carbonic acid.
  - D.—See Calcium Salts and Carbonates.
- P.—Dissolved in hydrochloric acid, the liquid should give no precipitate with potassium ferrocyanide denoting absence of iron.
  - U.- Employed in the manufacture of other calcium compounds.

## Calcium Iodide, -CaI2

- C.L.—Prepared like the corresponding barium compound, employing instead of a solution of barium one of calcium hydroxide.
- A.—Occurs in deliquescent needles, usually coloured brown by the presence of a little free iodine.
- S.—Freely soluble in water, insoluble in alcohol, slightly soluble in ether.
  - D.—See Calcium Salts and Iodides.
  - U.—Employed in collodion.

#### Calcium Salts, Tests for.

Soluble calcium salts are distinguished by the following reactions:—(1) Ammonium oxalate gives a white precipitate. (2.) Sulphuric acid gives a white precipitate in concentrated solutions. (3.) Ammonium carbonate preceded by ammonium chloride and ammonium hydroxide gives a white precipitate. (4) Mixed with hydrochloric acid and heated on platinum wire in the colourless flame of the Bunsen burner they colour it brick red.

## Camphor.— $C_{10}H_{16}O$ .

- C.—Obtained by carefully heating the wood of the camphor laurel (*Laurus camphora*) and collecting the volatile oil, which solidifies on cooling. The chief crude supplies come from China, and are resublimed before finding their way into commerce.
- A.—Occurs in white, translucent, tough masses, having a powerful and characteristic odour.
- S.—Almost insoluble in water, freely soluble in alcohol. Melted camphor dissolves pyroxilin (q.v.)
  - D.—Sufficiently identified by its appearance, etc.
- U.—Used in the manufacture of celluloid (vide Pyroxilin), and is an ingredient of certain retouching media. It is also occasionally employed to preserve gelatine and albumen from decomposition. A solution of it in alcohol was formerly much used to clear decolorised silver sensitising baths, but it has latterly been supplanted for this purpose by kaolin.

## Canada Balsam.

- C.—The resinous mass obtained by scoring the bark of the *Pinus balsamea*, a native of Canada and North America, whence it is imported (*vide* Turpentine).
- A.—Occurs as a pale yellow, ductile resin of the consistency of honey, and having an agreeable resinous smell.
  - S.—Insoluble in water, miscible in all proportions with alcohol.
- U.—Employed in certain varnishes, and sometimes used to render paper translucent.

## Carbon Dioxide.—CO<sub>2</sub>

Syn., Carbonic Acid.

- C.L.—Prepared by placing fragments of marble or limestone in an apparatus similar to the one used in making sulphuretted hydrogen (q.v.), and pouring hydrochloric acid diluted with six times its volume of water through the thistle funnel. Whiting, chalk, or even common washing soda may be substituted for the marble. The gas should be washed before use by passing it through a little water.
- A.-A colourless, odourless, heavy gas, extinguishing a taper and turning lime-water milky.

S.—Soluble to a slight extent in water, the solution being looked upon as true carbonic acid formed thus,  $CO_0 + H_0O = H_0CO_3$ .

U.—Employed in the manufacture of several other substances.

#### Carbonates, Tests for.

(1.) All carbonates effervesce when treated with hydrochloric acid, and the gas evolved turns lime-water milky. (2.) The soluble carbonates give with barium nitrate a white precipitate soluble with effervescence in hydrochloric acid. (3.) The soluble carbonates give with silver nitrate a white precipitate soluble in nitric acid.

#### Carbon Disulphide.—CS<sub>2</sub>

- Syn., Sulphocarbonic Acid, Thiocarbonic Acid, Carbon Bisulphide, Sulphide, or Sulphuret of Carbon.
- C.- Made commercially by passing sulphur vapour over red-hot charcoal.
- L.—The commercial product often contains free sulphur, from which it can be freed by distillation, and certain volatile organic sulphur compounds, which impart to it a most disagreeable odour. It can be freed from these latter by shaking it up with finely-powdered mercuric chloride (corrosive sublimate) and then redistilling it with to fits volume of olive oil.
- A.—Occurs as a colourless, very volatile and inflammable liquid, slightly heavier than water, and having, when pure, a rather pleasant vinous smell. As not only the liquid but its vapour are exceedingly inflammable, and as a mixture of the vapour and air form a highly explosive mixture, special care must be taken in experimenting with it. The liquid and vapour are also highly poisonous.
  - S.—Insoluble in water. Dissolves amber and certain other resins.
  - D.—Safficiently identified by its smell, etc.
  - U.—Employed as a solvent for amber in making cold varnish.

#### Castor Oil.

- C.L.—Made by expressing the seeds of the castor oil plant (*Ricinus communis*). Imported from Calcutta, various parts of America, and the West Indies.
- A.—A thick, oily liquid. The purer kinds are pale yellow; inferior varieties of a darker colour. "Cold drawn" oil is much less liable to become rancid than those varieties prepared by heat.
  - S.—Insoluble in water, soluble in ether and alcohol
- U.—Employed in collodion to toughen it for enamelling purposes, and enters into the composition of certain retouching media.

## Catechol.—C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>

Syn., Pyrocatechin, Brenzcatechin, Oxyphenic Acid.

An isomer of resorcin and quinol.

C.L.—Obtained by fusing phenol-sulphonic acid with caustic potash  $C_6H_5SO_2OH + KOH + O_2 = C_6H_4(OH)_2 + KHSO_4$ . It also occurs as a bye-product in the manufacture of quinol.

A .- Met with in brownish or white prismatic crystals.

S .- Soluble in water, alcohol, and ether.

D.—(1.) It precipitates red cuprous oxide from an alkaline solution of copper tartrate (Fehling's solution). (2.) It reduces silver nitrate in the cold. (3.) Rendered alkaline its solutions rapidly become brown. (4.) It gives with ferric chloride a green colour, changed to red by the addition of a drop of a 10% solution of oxalic acid.

U.-Employed in alkaline development.

# Cellulose.— $(C_6H_{10}O_5)n$ .

The substance composing the cell-walls of plants. Cotton, linen, hemp and flax are commercial varieties of it.

Cotton wool which has been boiled with sodium carbonate to free it from resinous matter is nearly pure cellulose, and Swedish filtering paper one of the purest varieties of it. Paper, being made from rags, consists essentially of cellulose.

D.—Strong, cold sulphuric acid changes cellulose into a gum-like substance; the hot acid converts it first into dextrin and then into dextrose, which latter will yield alcohol on fermentation.

Dilute cold sulphuric acid converts it into its isomeride anyloid—a property turned to account in making parchment paper by dipping unsized paper into strong sulphuric acid, mixed with half its volume of water, and carefully cooled. A solution of zinc chloride acts in a similar way.

As amyloid, unlike cellulose, is turned blue by iodine, cellulose can be detected by boiling it with zinc chloride and adding a solution of iodine to the product.

Left for some hours in contact with strong sulphuric acid, cellulose is converted into hydrocellulose, readily soluble in hot alkalies. This reaction is turned to account in recovering wool, as shoddy, from old rags.

Nitric acid converts cellulose into a series of cellulo-nitrins, which are treated of in another place (vide Pyroxilin).

U.—Cellulose as cotton wool, etc., is employed in photography to manufacture pyroxilin. If cotton wool is used, that known as long-fibre Sea Islands cotton is preferred by most makers.

## Charcoal, Animal.

Syn., Bone Black.

C.L.—Obtained by heating crushed bones in iron retorts. Occurs as a bye-product in the manufacture of Dippel's oil, as the oily liquid obtained by treating bones in this way is called. The black residue contains about 1 per cent. of carbon in a very fine state of division, the remainder being calcium phosphate.

A.—Occurs in hard black lumps.

S.—Insoluble in water, partly soluble in hydrochloric acid.

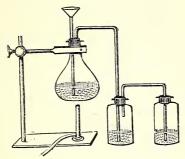
D.—The substance treated with hydrochloric acid leaves a black residue of carbon, and the filtrate gives a white precipitate when supersaturated with ammonia.

U.—Employed to deodorise offensively-smelling albuminised paper made from blood albumen.

#### Chlorine.-Cl.

C.—Prepared by acting upon manganese peroxide with hydrochloric acid  $MnO_2+4HCl=2H_2O+Cl_2+MnCl_2$ , or by acting upon a mixture of manganese peroxide and common salt with sulphuric acid  $2NaCl+MnO_2+2H_2SO_4 = Na_2SO_4+MnSO_4+2H_2O+Cl_2$ .

L.—On a small scale chlorine water may be prepared thus: Mix 18 parts of coarse kitchen salt with 15 parts of finely powdered manganese peroxide. Place the mixture in a flask provided



with a thistle funnel and exit tube and connected with a small bottle, half-filled with water and furnished with glass tubes as shown, and connected to another bottle half-full of water. The flask being in position on the ring of the retort stand pour in through the thistle funnel a cold mixture of 45 parts of strong sulphuric acid and 21 parts of water. On gently shaking the flask the chlorine is disengaged slowly and regularly, and when the evolution of gas slackens heat may be applied. Owing to the suffocating smell of chlorine the entire operation must be performed out of doors or in a chimney flue.

A .-- A greenish-yellow suffocating gas.

S.—Slightly soluble in water and soluble with decomposition in alcohol.

U.—Employed in the manufacture of many photographic substances. A solution of it in water has been recommended as a hypo eliminator, the reaction being similar to that which occurs with bromine (q.v.)

## Chlorates, Tests for.

(1.) Any solid chlorate mixed with a drop of strong sulphuric acid, and gently heated, gives rise to a series of small explosions, due to the formation and decomposition of chlorine peroxide gas (Cl<sub>2</sub>O<sub>4</sub>). (2.) When strongly heated for some time, chlorates are decomposed into chlorides, and the solution now gives a white precipitate with silver nitrate. (3.) A solution of a chlorate, mixed with a little sulphuric acid, will change to yellow the orange colour of an alcoholic solution of aurine.

## Chlorides, Tests for.

(1.) Any solid chloride, heated with manganese peroxide and strong sulphuric acid, liberates chlorine, which bleaches red litmus paper, and turns paper moistened with starch and potassium iodide blue. (2.) Any chloride, heated with potassium dichromate and sulphuric acid, liberates red vapours of chloro-chromic anhydride. (3.) Any soluble chloride gives with silver nitrate a white curdy precipitate, insoluble in water and in nitric acid, but soluble in ammonium hydroxide. (4.) Any soluble chloride gives with lead nitrate a white precipitate slightly soluble in cold and very soluble in boiling water. (5.) Any soluble chloride gives with mercurous nitrate a white precipitate blackened by ammonium hydroxide.

Chlorides in presence of iodides and bromides are best detected by completely precipitating with silver nitrate and digesting the well-washed precipitate with 10 % ammonium hydroxide, when, if a chloride was originally present, the filtrate will be turned

milky on supersaturating it with nitric acid.

## Copal.

C.—A resinous substance coming from Zanzibar, the West Coast of Madagascar, and the East and West Coasts of Africa. It occurs as a fossilised or fresh resin. Little is known of the genus or species of the tree yielding the former kind, but the latter is commonly attributed to the Trachylobium mossambicense. The fossil resin occurs in red, sandy soil, or in stiff, blue clay, and is obtained from excavations made in a very primitive manner with a pointed stick. The fresh variety is either picked directly from the tree or gathered from the loose soil in which it is embedded. True or ripe copal is exclusively fossil, the fresh variety being considered of poorer quality. The resin is, after gathering, usually cleaned by boiling with dilute alkali.

A.—Occurs in clear or opaque pieces, of which the former are

best.

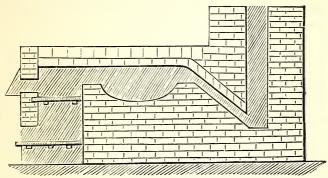
S.—Insoluble in water and not very soluble in alcohol, but the addition of a little camphor enables it to be dissolved more readily. Long keeping also increases its solubility, probably by oxidising it more or less, and the same object is rapidly attained by melting it at as low a temperature as possible, dropping it in a molten condition into water, finely powdering the brittle tears so obtained, and drying the powder very thoroughly. It is freely soluble in chloroform and ether.

U.—Occasionally employed in varnish making.

## Copper.—Cu.

Occurs abundantly in nature as copper pyrites (CuFeS<sub>2</sub>), malachite (CuCO<sub>3</sub> Cu(OH)<sub>2</sub>), etc. The former is met with in various parts of the United Kingdom, the latter in Australia, from which country it is largely exported to Swansea, the seat of the copper trade.

C.—The processes involved in the extraction of copper from pyrites are practically five in number. (1.) Roasting the ore to expel extraneous volatile matters, and to convert the greater part of the iron into ferric oxide (Fe $_2$ O $_3$ ) and the copper into cupric oxide (CuO). (2.) Fusing the product obtained in (1) to remove the greater part of the iron as fusible ferrous silicate (FeSiO $_3$ ). (3.) Strongly heating the product obtained in (2), when blister copper is obtained Cu $_2$ S + 2CuO = SO $_2$  + 2Cu $_2$ . (4) Refining the blister copper from (3) by strongly heating it in a current of air to remove the last traces of foreign substances. (5.) Toughening or poling the "dry" copper from (4) by stirring it with a pole of green wood. The first four operations are carried out in a reverberatory furnace.



L.—Perfectly pure copper may be obtained by passing a current of electricity from four Grove's cells (or other cells of equivalent power) through a solution of copper sulphate, using electrodes of platinum.

A.—A red metal somewhat soft and practically unacted upon by the atmosphere. Occurs in many forms in commerce, of which the best for chemical purpose is fine copper tacks. Pure copper obtained by electrolysis is supplied by most dealers.

S.—Dissolves very slowly in dilute sulphuric acid, but rapidly in the concentrated boiling acid, yielding copper sulphate  $(CuSO_4)$  and sulphide (CuS), and liberating sulphur dioxide gas  $(q \ v.)$ 

Nitric acid, concentrated or dilute, acts upon it at once, converting it into copper nitrate Cu(NO<sub>3</sub>)<sub>2</sub>. Boiling hydrochloric acid slowly converts it into cupric chloride CuCl<sub>2</sub>.

D.—Sufficiently identified by its appearance.

U.—Employed to precipitate silver from old cyanide or hypo fixing baths. It fulfils this function owing to the fact that it is more readily attacked by potassium cyanide or by hypo than metallic silver.

A solution of cupric oxide (CuO) in ammonia is employed to waterproof paper and cardboard, the material being then known as "Willesden paper." Paper so waterproofed is employed in practical photography for a variety of purposes, ranging from a studio to a dish. It cannot, however, be used for fixing solutions, as/hypo or cyanide dissolve out the copper oxide.

## Copper Salts, Tests for.

Soluble copper salts give the following reactions:—(1.) With sulphuretted hydrogen, a black precipitate, soluble in nitric acid. (2.) With ammonium hydroxide, a greenish blue precipitate, soluble in excess to a blue liquid. (3.) With potassium ferrocyanide, a reddish brown precipitate. (4.) With sodium hydroxide, a pale blue precipitate, changing to black on boiling. (5.) With potassium iodide, a drab-coloured precipitate.

## Cupric Sulphate.— $CuSO_4 + 5H_2O$ .

Syn., Copper Sulphate, Sulphate of Copper, Blue Stone, Blue Vitriol, Blue Copperas.

C.—Manufactured by roasting copper pyrites (CuFeS<sub>2</sub>) at a high temperature with free access of air, when a mixture of ferrous and cupric sulphate first results  $FeCuS_2 + 4O_2 = FeSO_4 + CuSO_4$ , but the ferrous sulphate is then decomposed thus,  $2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$ , the copper sulphate remaining unchanged.

On treating the mass with water the cupric sulphate dissolves and the ferric oxide remains behind, and the solution yields cupric sulphate on evaporation.

- L.—A pure product can be obtained from the commercial varieties by repeated recrystallisation.
- A.—Occurs in blue crystals, which, if large and well formed, are practically pure.
  - S.—Soluble in twice its weight of cold water, insoluble in alcoho!.
  - D.—See Copper Salts and Sulphates.
- P.—Frequently contains more or less ferrous sulphate, detected by adding an excess of ammonium hydroxide to a solution of it, when, if iron is present, a residue will remain.
- U.—Employed, mixed with solutions of ferrous sulphate, to retard the oxidation of the latter.

## Cupric Bromide.—CuBr<sub>2</sub>

Syn., Bromide of Copper.

- C.L.—Made by dissolving cupric oxide in hydrobromic acid and evaporating down the solution  ${\rm CuO} + {\rm 2HBr} = {\rm H_2O} + {\rm CuBr_2},$  or by mixing solutions of cupric sulphate and potassium bromide  ${\rm CuSO_4} + {\rm 2KBr} + {\rm K_2SO_4} + {\rm CuBr_2}.$  In the latter case the solution should be evaporated to small bulk and cooled, when the slightly soluble potassium sulphate will separate out.
  - A.—Occurs in deliquescent light blue needles.
  - S.—Extremely soluble in water, insoluble in alcohol.
  - D.—See Copper Salts and Bromides.

U.—Used as a collodion intensifier to convert the silver image into insoluble silver bromide and cuprous bromide; thus,  $2Ag + 2CuBr_2 = 2AgBr + Cu_2Br_2$ . The bleached image is then treated with a solution of silver nitrate, when the cuprous bromide is converted into silver sub-bromide and cupric nitrate  $Cu_2Br_2 + 4AgNO_3 = 2Cu(NO_3)_2 + 2Ag_2Br$ .

### Cyanides, Tests for.

(1.) Solid cyanides, acted upon by dilute hydrochloric acid, liberate hydrocyanic acid, readily recognisable by its smell. (2.) Solid cyanides fused with sodium thiosulphate (hypo) are converted into sulphocyanates, detected by dissolving the fused mass in water and adding ferric chloride, when a blood red colour will be produced. Solutions of cyanides give the following reactions:

(3) With silver nitrate a white precipitate soluble in ammonia.

(4.) With ferrous sulphate, followed by ferric chloride, caustic soda and hydrochloric acid, they yield a blue solution.

### Cyanin lodide.—C<sub>28</sub>H<sub>35</sub>N<sub>2</sub>I.

Syn., Cyanin, Quinolin or Chinolin Blue, Quinolin-cyanin,

C.L.—Prepared by making a mixture of 60 parts glycerin, 19 parts anilin, 12 parts nitro-benzene, and 50 parts Nordhausen sulphuric acid, and heating the whole to 130°C. for about three hours in a flask provided with an inverted condenser (see page 41). At the end of this period the condenser is removed, and the product heated for three hours, or until fumes cease to be evolved. The liquid is finally poured over an excess of lime contained in a hard glass retort and distilled. The mixture of quinolin and anilin so obtained is then redistilled in a retort provided with a thermometer, the distillation being stopped when the thermometer indicates 190°C. By this means the quinolin, which boils at 240°C., is left behind. This is then fused with amyl iodide and caustic potash, and the fused mass treated with alcohol, which dissolves out the cyanin, from which solution it can be obtained by evaporation.

- A.—Occurs as a dark blue powder.
- S.—Slightly soluble in water, fairly soluble in a'cohol.

U.—Employed in orthochromatic photography for increasing the sensitiveness of silver bromide to the red end of the spectrum. As it is extremely sensitive to light, solutions of it should be kept in the dark.

D.—Hydrochloric acid decolorises it, and ammonia restores the colour. When sufficiently dilute, light bleaches its solutions.

#### Dammar.

### Syn., Gum Dammar.

- C.—A re-inous substance, of which four varieties are met with in commerce. (1.) East Indian dammar, obtained from the Amboyna pine (Dammara orientalis), and being the natural exudation of the tree. This variety is imported from Amboyna, and occurs in straw-coloured more or less transparent masses, the exterior surface of which is coated with a white powder. (2.) Sal dammar, obtained from the sal tree (Vatica robusta) of Borneo, Sumatra and Central India. It occurs in yellow, brittle, nearly opaque pieces. (3.) Black dammar, got from the Canarium strictum of the Tinevelly district of India. Occurs in large black lumps. (4.) Rock dammar, got from the Hopea odorata of Rangoon and the Hopea micrantha of Malacca. It forms pale straw-coloured nodules rather less brittle than the East Indian variety, but otherwise much resembling it.
- S.—All these varieties are more or less soluble in turpentine, alcohol, chloroform, carbon disulphide, benzole and petroleum spirit, the second variety yielding a turbid solution and the third a dark-coloured one.
- U.—East Indian and rock dammar form the basis of many photographic varnishes. Of these the latter is to be preferred, as it is rather more soluble than the former, and gives a harder and more durable varnish. A dilute solution of dammar in turpentine is often used as a retouching medium.

# **Dextrin.**— $(C_6H_{10}O_5)n$ . Syn., British Gum.

- C.L.—Made by moistening starch with one-third of its weight of water, containing 66 % of nitric acid, air-drying the pasty mass and then heating it for some time to 115°C.
  - A.—Occurs as a brownish powder.
  - S.—Readily soluble in hot water.
  - U.—Employed as a mountant.

### Diazobenzene Sulphonic Acid. - C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>N<sub>2</sub>.

- C.L.—Made by heating benzene to dryness with strong sulphuric acid and sand, dissolving the residue in a mixture of caustic soda and potassium nitrite, and pouring the solution into dilute sulphuric acid, when the substance is thrown down as a nearly white powder.
  - U.—Employed in the manufacture of methyl crange.

### Eosin.

A generic term used to denote a series of products derived from fluorescein (q.v.)

### Chloroform.—CHCl<sub>3</sub>

- C.—Prepared on a large scale by distilling a mixture of bleaching lime and slaked lime with alcohol or methylated spirit and water. The following equation is believed to represent the change:  $8\text{CaCl}_2\text{O}_2 + 4\text{C}_2\text{H}_5\text{OH} = 2\text{CHCl}_3 + 3\text{Ca}(\text{O}_2\text{CH})_2 + 5\text{CaCl}_2 + 8\text{H}_2\text{O}, \text{ the calcium formate } (\text{Ca}(\text{O}_2\text{CH})_2) \text{ and calcium chloride } (\text{CaCl}_2) \text{ remaining behind, and the chloroform } (\text{CHCl}_3) \text{ distilling over.}$
- L.—On a small scale the process may be carried out thus: Introduce into a gallon tin oilcan 16 ozs of bleaching lime and six ounces of finely-powdered quicklime, previously slaked with two ounces of water. Pour over the mixture three ounces of rectified spirits of wine (or of methylated alcohol) and 50 ozs of water. Shake the contents of the vessel well, and having connected the can with a condenser supplied with ice-cold water, distil at a gentle heat until five ounces have been collected. Shake the distillate in a stoppered bottle with its own volume of water and set aside for a short time, when the mixture will separate into two layers, the lower of which is chloroform. Decant off the water and repeat the process three times. Then shake up the liquid with its own volume of strong sulphuric acid and decant off the chloroform, which will now float at the top. Finally, re-distil it, first alone, and lastly over fused calcium chloride.
- A.—A colourless, pleasant smelling, heavy liquid. As it boils at 60°C. it is advisable to keep it in an accurately stoppered bottle, and in a cool place.
- S.—Insoluble, or nearly so, in water, fairly soluble in alcohol, ether, and turpentine. It dissolves caoutchouc, mastic, copal, amber, and other resinous substances
- D.—Chloroform heated with sodium hydroxide and anilin sulphate evolves the highly characteristic and offensive odour of phenyl carbamine  $(C_6H_5NH_2)$ .
- P.—If water is present, the sample will evolve hydrogen gas on being poured over a pellet of metallic sodium. If alcohol is present, a drop of it poured into water will become opalescent.
  - U.—Employed as a solvent for amber, etc.

### Chlorophyl.

The name applied to the green colouring matter of plants.

- L.—It can be extracted by digesting the finely chopped leaves with warm alcohol for a few minutes, and at once filtering the solution. It is best used fresh, but keeps fairly well in the dark and in contact with a little zinc dust
- U.—Employed in orthochromatic photography to render silver bromide, etc., more sensitive to the rays at the red end of the spectrum.

### Chloroplatinous Acid.—H2PtCl4

Syn., Bichloride of Platinum, Platinous Chloride.

C.L.—Made by carefully heating chloroplatinic acid to about 300°C., when the true platinous chloride PtCl, is obtained, which on the addition of hydrochloric acid yields the substance in question. The change is more conveniently brought about by sulphur dioxide (SO<sub>2</sub>), in the following way: Chloroplatinic acid is dissolved in twice its weight of water, and the filtered solution heated on a water bath, and a rapid current of well-washed sulphur dioxide passed through it. As soon as the yellow solution has changed to a distinct red, a drop of it is taken out on a glass rod and mixed in a watch glass with a drop of a concentrated cold solution of ammonium chloride. If an immediate yellow precipitate is produced, the sulphur dioxide is permitted to act upon the solution for a little longer. Every five minutes or so the test is re-applied and the current of gas stopped, when the yellow precipitate ceases The change is represented thus, H<sub>2</sub>PtCl<sub>6</sub>+SO<sub>2</sub>+ to form. 2H<sub>2</sub>O=2HCl+H<sub>2</sub>SO<sub>4</sub>+H<sub>2</sub>PtCl<sub>4</sub>. If the current of sulphur dioxide is continued for too long a time the chloroplatinous acid becomes converted into platinous sulphite thus H<sub>2</sub>PtCl<sub>4</sub> + SO<sub>2</sub> + H<sub>2</sub>O = PtSO<sub>3</sub>+4HCl.

U.—The solution obtained as above is converted into potassium chloroplatinite (q.v.), used in the platinotype process.

### Chloroplatinic Acid.—H<sub>2</sub>PtCl<sub>6</sub> + 6H<sub>2</sub>O.

Syn., Platinic or Platinum Chloride, Chloride or Perchloride of Platinum, Muriate of Platina.

C.L.—Prepared by dissolving metallic platinum at a gentle heat in aqua regia, 100 grains of platinum requiring for solution two and a-half measured ounces of the liquid. The change is represented thus:  $2\text{HNO}_3 + 8\text{HCl} + P\text{t} = 4\text{H}_2\text{O} + 2\text{NOCl} + \text{H}_2\text{PtCl}_6$ . When the platinum is dissolved the solution should be evaporated to small bulk, some hydrochloric acid added to it, and the evaporation repeated so as to expel all the free chlorine. On finally evaporating the liquid to a thick syrup and permitting it to stand for some time the chloroplatinic acid will separate out.

A.—Occurs as a dark brownish red, very deliquescent, more or less crystalline mass.

S.—Freely soluble in water and alcohol.

D.—See Platinum Salts.

U.—The solution serves as a test for potassium and ammonium, with which it forms sparingly soluble precipitates of potassium and ammonium chloroplatinate (K<sub>2</sub>PtCl<sub>6</sub>, (NH<sub>4</sub>)<sub>2</sub>PtCl<sub>6</sub>). It is also the starting point in the manufacture of potassium chloroplatinite (q.v.)

## Chromic Anhydride.—CrO<sub>3</sub>

Syn., Chromium Trioxide, Chromic Acid.

C L.—Made by adding to one volume of a saturated solution of potassium dichromate in boiling water cooled down to 50° C. a volume and a half of strong sulphuric acid in small quantities at a time—when, on cooling, crystals of chromic anhydrice separate out. These are collected on a funnel plugged with asbestos or glass wool (cotton wool or paper would be at once attacked), drained, washed repeatedly with strong nitric acid until the washings, when diluted with water, cease to give a precipitate with barium nitrate, and then transferred to a dish and heated until they melt. The fused mass is finally broken up, whilst still warm, and rapidly transferred to a stoppered bottle.

A.—Occurs in a confused mass of brownish red, highly deliquescent crystals.

D.—When dissolved in water, it yields a red solution, which neutralised with ammonium hydroxide gives the reactions of the chromates (q.v.) The solid ignites strong alcohol dropped upon it and becomes converted into chromic oxide  $(\operatorname{Cr}_2\operatorname{O}_3)$ , the alcohol being oxidised to acetic acid in accordance with the equation  $3\operatorname{C}_2\operatorname{H}_5\operatorname{OH} + 4\operatorname{CrO}_3 = 3\operatorname{C}_2\operatorname{H}_4\operatorname{O}_2 + 3\operatorname{H}_2\operatorname{O} + 3\operatorname{Cr}_2\operatorname{O}_3$ .

U.—Used in the preparation of ammonium bichromate.

### Chromium Potassium Sulphate.— $KCr(SO_4)_2 + 12H_2O$ .

Syn., Chrome Alum.

C.—Prepared on a large scale as a bye-product in the manufacture of alizarin from anthracene, in which process the latter substance is treated with a mixture of potassium bichromate and sulphuric acid to oxidise it.

L.—On a small scale it may be made from potassium bichromate by any of the following processes:—(1.) By boiling it with a large excess of strong sulphuric acid thus, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>  $+ 4H_2SO_4 = 2 KCr(SO_4)_2 + 4H_2O + O_3$ . (2.) By passing sulphur dioxide gas through a solution of potassium bichromate acidulated with sulphuric acid,  $K_2Cr_2O_7 + 3SO_2 + H_2SO_4 =$  $2KCr(SO_4)_2 + H_2O$ . (3.) By boiling a mixture of potassium bichromate, sulphuric acid and alcohol,  $2K_2Cr_2O_7 + 3C_2H_5OH + 8H_2SO_4 = 11H_2O + 4KCr(SO_4)_2 + 3C_2H_4O_2$ . The latter process is conveniently carried out on a small scale by dissolving three ounces of potassium dichromate in ten ounces of boiling water, and gradually adding to the mixture four and a half ounces of strong sulphuric acid, followed by half-ounce of pure alcohol added drop by drop from a separating funnel. The liquid is finally reduced to five ounces by evaporation and set aside for two days, when crystals will separate out. These should be washed with cold water to free them from adhering sulphuric acid.

A.—Occurs in dark violet, octahedral, permanent crystals.

- S.—Soluble to a purple solution in seven times its weight of cold water. Hot water gives a green solution, which, after several days, changes to purple. The salt cannot be crystallised from this green solution.
  - D.—See Chromium Salts, Potassium Salts, and Sulphates.

U.—Employed with gelatino-bromide plates to prevent frilling, and also used in many photo-mechanical processes. Its use for these purposes depends upon the fact that it renders gelatine insoluble in, although still capable of absorbing, water.

### Chromates, Tests for.

(1.) Solid chromates heated with sulphuric acid and common salt yield red vapours of chromium oxychloride. Solutions of chromates give the following reactions:—(2.) Barium nitrate produces a yellow precipitate. (3.) Silver nitrate a dark red precipitate. (4.) Lead n trate a yellow precipitate. (5.) Sulphuretted hydrogen or sulphur dioxide change the yellow or red colour of the solution to green.

## Chromium Salts, Tests for.

Soluble salts containing chromium give the following reactions:—(1.) Ammonium hydroxide or ammonium sulphide gives a greenish blue precipitate, insoluble in excess. (2.) Sodium hydroxide a similar precipitate, soluble in excess. (3) Sodium phosphate a greenish white precipitate.

### Citric Acid.—C6H8O7+H2O.

C — Occurs naturally in bergamot, lime and lemon juice, from which it is obtained by heating the juice to about 100 °C. and adding whiting until effervescence ceases. The liquid is then set aside for some time, when calcium citrate separates out as an insoluble white precipitate,  $2C_6H_8O_7 + 3CaCO_3 = 3CO_2 + 3H_2O_3 + Ca_3(C_6H_5O_7)_2$ . This is carefully washed with cold water and decomposed by sulphuric acid thus,  $Ca_3(C_6H_5O_7)_2 + 3H_2SO_4 = 3CaSO_4 + 2C_6H_8O_7$ . The liquid filtered from the insoluble calcium sulphate is then concentrated in a vacuum pan under greatly diminished pressure to avoid charring and loss of acid, and set aside to crystallise.

- A.—Met with in commerce as white, transparent, permanent crystals.
- S.—Dissolves in half its weight of boiling water, and in its own weight of alcohol.
- D.—Neutralised with caustic soda it becomes converted into sodium citrate, which responds to the usual tests. (See Citrates, Tests for.)
- P.—The commercial product is frequently adulterated. Sulphuric acid is detected by adding a large excess of hydrochloric acid, followed by barium chloride, when a white precipitate will

occur if sulphuric acid is present. Tartaric acid is detected thus: (1.) A strong solution of the acid is mixed with an excess of caustic soda, and sufficient potassium permanganate added to the liquid to colour it a light pink. If the mixture is boiled, it will become brown if tartaric acid is present. (2.) A saturated alcoholic solution of the acid is mixed with an equal volume of a saturated alcoholic solution of potassium acetate, and vigorously shaken; when, if tartaric acid is present, a white crystalline precipitate will gradually form. Lead is sometimes present, and is readily detected by sulphuretted hydrogen. Oxalic acid is occasionally, though rarely, used as an adulterant, and can be detected by supersaturating a solution of the acid with ammonia, reacidifying with acetic acid, filtering if necessary, and adding a solution of calcium sulphate, when a white precipitate will fall if oxalic acid is present.

U.—Employed to prepare various citrates and to "preserve" sensitised paper.

## Citrates, Tests for.

Solid salts strongly heated blacken and give off irritating fumes. Solutions give the following reactions:—(1.) With calcium chloride or lime-water a white precipitate on boiling or on standing for a considerable time. (2.) With silver nitrate a white precipitate not blackened on boiling.

# Eikonogen. $-C_{10}H_5NH_2ONaHSO_3+2H_2O.$

Syn., Sodium Amido Beta Naphthol Beta Sulphonate.

- C.L.—The acid itself can be prepared by the reduction of nitroso beta naphthol sulphonic acid, or of the orange colouring matter obtained by acting upon diazobenzene chloride with Schäffer's beta naphthol beta sulphonic acid.
- A.—The acid itself (sold as "Anglol") is met with in brownish crystals, the sodium salt (eikonogen) in yellowish white ones.
- S.—Sparingly soluble in water, insoluble in alcohol. The aqueous solution becomes yellow, and finally brown, through absorption of oxygen. The addition of sodium sulphite causes the oxidising solution to change to green instead of brown.
- D.—Barium nitrate gives a white precipitate which usually does not form for ten seconds or so. A trace of mercuric chloride gives a black precipitate, becoming violet on boiling, and dissolving to a claret red solution in an excess of nitric acid, red nitrous fumes being meanwhile evolved. This red solution becomes turbid on diluting it considerably with water. An excess of mercuric chloride gives a greyish white or greenish precipitate, gradually changing through various shades of orange to deep brown.
- U.—Employed for the same purposes as pyrogallol, quinol etc., over which it is said to possess the advantage of being non-poisonous.

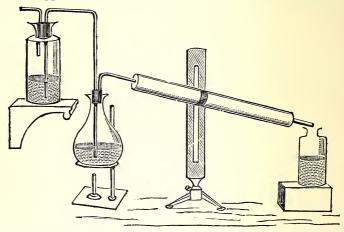
## Ethylic Oxide.—(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O.

Syn., Ether.

C.L.—Prepared by distilling ethylic alcohol with sulphuric acid. The alcohol is first converted by the acid into sulphethylic acid thus,  $C_2H_5OH + H_2SO_4 + C_2H_5HSO_4 + H_2O$ , and this then acts upon a fresh portion of the alcohol to form ether and sulphuric acid  $C_2H_5HSO_4 + C_2H_5OH = (C_2H_5)_2O + H_2SO_4$ .

It is clear from the equations that a small quantity of sulphuric acid will suffice to convert a large quantity of alcohol in ether, continuing to do so, in fact, until the water, which is a necessary result of the action, has so diluted it as to render it incapable of bringing about the change.

On a comparatively small scale ether may be conveniently made in the apparatus figured in the text. In the flask, disconnected



from the condenser and placed, if possible, in ice-cold water, 12 ounces of rectified spirit are mixed in small quantities at a time with 10 ounces of strong, pure sulphuric acid, every care being taken to prevent a sudden rise of temperature. The flask is then connected as shown, and a paper band gummed round it to mark the level of the inclosed liquid. In the bottle supported on a shelf 30 ounces of rectified spirit have meanwhile been introduced. The flask and contents are now slowly raised to the boiling point, and when the ether begins to distil over fresh alcohol is introduced by blowing into the tube connected with the bottle, and which should be drawn out to a fine point so as to permit the alcohol to be delivered drop by drop. The liquid in the flask should, during the whole time, be maintained at the same level. When the whole of the alcohol has been transferred from the bottle to the flask the operation is at an end.

The liquid in the receiver contains ether, alcohol, water and sulphurous acid. To purify the ether, the whole is transferred to a large stoppered bottle and well shaken up with cold water added in quantities of an ounce at a time, the addition being continued so long as the layer of ether floating on the top is seen to increase in volume. About a drachm of caustic sodium dissolved in a little water is next added, and the liquid vigorously agitated. After an hour or so the ether is decanted or syphoned off into a large flask half full of fused calcium chloride and permitted to stand for twelve hours or more, after which it is redistilled on the water bath. The product will be pure and nearly anhydrous ether of specific gravity 72. If methylated spirit is substituted for rectified spirit the product is known as methylated ether, and answers quite as well as the pure product for every photographic purpose. To dehydrate ether it is only necessary to mix it with half its bulk of quicklime, let the whole stand for a week and filter the mixture.

A.—Ether is a volatile, colourless, inflammable liquid, having a characteristic pleasant odour. On account of its low boiling point (35° C.) it must be kept in a cool place, and in a well-stoppered bottle. As its vapour is not only inflammable, but, when mixed with air, explosive, special care must be taken when using it, or substances such as collodion, etc., at night.

P.—Ether sold as pure is liable to contain methylated ether, water, alcohol and oxidation products due to long keeping.

Methylated ether is detected by adding a drop of tincture of iodine to the sample, when, if quite pure, the colour will not be discharged even after some hours.

Alcohol is detected by shaking it up with water, decanting off the ether, and applying the iodoform test to the water. (Vide Alcohol.)

Oxidation products are detected by shaking up the sample with an aqueous solution of starch and potassium iodide, which will be blued if these are present. Water is detected by the turbidity produced when the sample is mixed with oil of turpentine or carbon disulphide, or by shaking it up with rosaniline acetate (fuchsine or magenta), when a red colour will be produced. Both water and alcohol can be removed from a sample of ether by letting it stand for some days in contact with fused calcium chloride.

U.—Employed in photography to make collodion. As light appears to oxidise ether, it is often difficult to obtain it free from oxidation products, the presence of which is shown when the collodion is made by a brown colour due to the liberation of iodine. This colour can be removed and the collodion restored to its original sensitiveness by shaking it up with filings of metallic cadmium. Ether containing much water appears to be gradually converted into alcohol, and eventually into acetic acid.

Owing to the fact that ammonium iodide is decomposed by acetic acid, collodion containing this salt, and made with a too weak sample of ether, very soon becomes brown, and continues to change in colour even after having been decolorised with metallic cadmium. As cadmium iodide is unaffected by acetic acid, collodions containing it do not change colour even when water is present, unless oxidation products, other than acetic acid, are present. Oxalic acid has been detected in very old samples of collodion, but this was probably derived, not from the ether, but from the pyroxilin.

As mixtures of ether and alcohol are frequently used in photography, the following tables due to Squibb will be found useful as enabling the percentage of each ingredient to be deduced from the specific gravity of the mixture.

Specific gravities of mixtures of absolute ether and alcohol, the ether having a spec. grav. at 15°C. of .719, the alcohol of .820:—

0 2 0	
Percentage of ether.	Specific gravity.
100	·7189
99	$\cdot 72021$
98	$\cdot 72152$
97	·72284
96	.72416
95	$\cdot 72541$
94	.72666
93	$\cdot 72792$
92	·72918
91	·73043
90	·73168
89	·7 <b>3</b> 298
88	$\cdot 73428$
87	•73547
86	•73666
85	•73785
84	·73904
83	•74022
82	•74141
81	·74260
80	•74378
79 70	·74495
78 77	$^{\cdot 74612}_{\cdot 74729}$
77 76	·74846
7.0 75	•74975
74	.75104
73	.75233
72	·75362
71	.75492
70	.75623
	,0029

# Ferric Ammonium Citrate.—Fe<sub>2</sub>(NH<sub>4</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>)<sub>3</sub> Syn., Ammonio-citrate of Iron.

C.L.—Mix in a 30 oz. flask four drachms of strong sulphuric acid with seven ounces of water, and having raised the liquid to boiling, dissolve six ounces of ferrous sulphate in it. Now add half-ounce strong nitric acid, diluted with two ounces of water, to the mixture, and continue boiling until the iron is completely oxidised, as is evidenced by its ceasing to give a blue precipitate with potassium ferricyanide. Next precipitate the iron completely with an excess of ammonia (vide Ferric Hydroxide), well wash the precipitate and boil it for five minutes with four ounces of citric acid dissolved in ten ounces of water. Filter the mixture, and when cool add to it 5½ oz. of ammonia, spec. grav. 96. Filter again, evaporate to dryness at 100° C., and keep the residue in a stoppered bottle.

- A.—Occurs in thin, almost transparent, brownish, slightly deliquescent scales.
  - S.—Freely soluble in water and in alcohol.
  - D.—See Tests for Ferric Salts, Ammonium Salts and Citrates.
  - P.—Is usually quite pure.
- U.—It becomes converted into a ferrous salt during exposure to light in contact with the organic matter of the paper on which it is spread, and is on that account used in several forms of the so-called "blue" process.

# Ferric Ammonium Oxalate.— $\operatorname{Fe_2(NH_4)_2}C_2O_4$ )<sub>4</sub>

Syn., Ammonio-oxalate of Iron.

- C.L.—Dissolve three ounces oxalate acid in eight ounces water, raise the solution to the boiling point, and saturate it with moist ferric hydrate (q.v.), avoiding a large excess. Filter the solution so obtained, add to it an ounce of oxalic acid dissolved in three ounces water and exactly neutralised with ammonia, filter again if necessary, and evaporate to dryness at 100°C.
- A.—Occurs in green crystals freely soluble in water. These are best kept in the dark, as light oxidises them more or less—a remark which also applies to ferric ammonium citrate
  - D.—See Tests for Ferric Salts, Ammonium Salts, and Oxalates.
  - P.—Usually quite pure.
- U.—Exposed to light, it becomes more or less converted into ferrous salt, and is on that account used in the platinotype and "blue" processes.

## Ferric Chloride.—Fe<sub>2</sub>Cl<sub>6</sub>

Syn., Perchloride of Iron.

C.L.—Dilute twelve ounces of strong hydrochloric acid with eight ounces of water, and add two ounces of fine pianoforte wire to the mixture, warming gently if necessary until the iron is all

dissolved, ferrous chloride being formed in accordance with the equation Fe+2HCl=2H+FeCl<sub>2</sub>. Filter the solution into a 40 ounce flask and add strong nitric acid to it in quantities of half a drachm at a time, boiling after each addition until the solution ceases to give a blue precipitate with potassium ferricyanide. The nitric acid converts the ferrous into ferric chloride thus, 6FeCl<sub>2</sub>+2HNO<sub>3</sub>+6HCl=3Fe<sub>2</sub>Cl<sub>6</sub>+2NO+4H<sub>2</sub>O. The large flask is absolutely necessary owing to the tumultuous disengagement of nitric oxide gas towards the end of the process. Finally transfer the liquid to an evaporating dish, boil it down to syrupy consistence, let it solidify, rapidly break up the resulting mass of ferric chloride, and transfer the pieces whilst still hot to a stoppered bottle.

A.—Occurs in yellowish brown deliquescent lumps, usually containing more or less water.

- S .- Freely soluble in water and in alcohol.
- D.—See Tests for Ferric Salts and for Chlorides.
- P.—Usually quite pure.

U.—Employed to manufacture other compounds, and to a small extent to reduce gelatino-bromide plates, which it effects probably by converting the silver into silver chloride in accordance with the equation  $\operatorname{Fe_2Cl_6} + 2\operatorname{Ag} = 2\operatorname{FeCl_2} + 2\operatorname{AgCl}$ . As silver chloride is soluble to a certain extent in ferric chloride, a slight reduction takes place without further treatment, and this may be increased by transferring the well-washed plate to a solution of hypo.

# Ferric Citrate.— $\operatorname{Fe}_2(C_6H_5O_7)_2$

Syn., Citrate of Peroxide of Iron.

- C.L.—Add moist ferric hydrate (q.v.) to a hot solution of citric acid as long as it continues to be taken up, filter the solution and evaporate to dryness, first over a naked flame, and finally when the solution becomes syrupy at 100° C.
  - A.—Occurs in thin, transparent reddish scales.
  - S .- Freely soluble in water.
  - D.—See tests for ferric salts and for citrates.
  - P.—Usually quite pure.
  - U.—Employed in the same way as ferric-ammonio citrate (q.v.)

### Ferric Hydroxide.—Fe<sub>2</sub>(OH)<sub>6</sub>

Syn., Ferric Hydrate, Hydrated Peroxide of Iron.

C.L.—In a 40 oz. flask mix six drachms of strong sulphuric acid with ten ounces of water, raise the mixture to the boiling point and dissolve eight ounces of ferrous sulphate in it. Next add nitric acid in quantities of half-a-drachm at a time, boiling after each addition, and continuing to add the nitric acid until the iron is all oxidised (vide ferric ammonium citrate). About two ounces

of strong nitric acid will be required for this. When the conversion of ferrous to ferric sulphate is complete, add ammonia to the hot solution as long as a precipitate continues to form, collect this on a filter, wash it with boiling water until the washings cease to precipitate barium nitrate, and transfer the pasty mass to a stoppered bottle. The action of the ammonia is represented thus:  $Fe_2(SO_4)_3 + 6NH_4OH = Fe_2(OH)_6 + 3(NH_4)_2SO_4$ .

A.—Occurs as a soft, reddish-brown pasty mass.

D.—Dissolved in sulphuric acid it yields a solution which gives the usual reactions of ferric salts (q.v.)

U.—Employed in photography to prepare certain compound ferric salts.

Ferric Oxalate.— $\operatorname{Fe}_2(C_2O_4)_3$ 

Syn., Oxalate of Peroxide of Iron.

- C.L In a 20 oz. flask mix half-a-drachm of strong sulphuric acid with an ounce of water, and, having raised the mixture to the boiling point, dissolve 556 grains of ferrous sulphate in it nitric acid in quantities of 10 drops at a time to oxidise the iron, and when the oxidation is complete, precipitate the iron with ammonia and wash the precipitate (vide ferric hydroxide). In the dark room, break the point of the filter paper with a glass rod and wash the ferric hydroxide into a beaker with a cold solution of 378 grains of oxalic acid dissolved in an ounce of water. Let the mixture stand for several days completely protected from light, and filter it when a solution containing 376 grains of ferric oxalate will be obtained. The action of the oxalic acid upon the ferric hydroxide is represented thus: Fe<sup>2</sup> (OH)6 +  $3C_2H_2^1O_4$  = Fe<sub>2</sub> ( $C_2O_4$ )3 +  $6H_2O$ . For use in the platinotype process, the liquid should contain 100 grains of ferric oxalate per ounce, so that the liquid obtained should be made up to 33 ounces in bulk by adding water to it, when it will be of that strength, about five grains of oxalic acid being added to it. During the solution of the ferric hydroxide in the oxalic acid it is best not to employ heat, otherwise a partial decomposition might occur. By evaporating the liquid under the exhausted receiver of an air-pump the salt can be obtained in the solid form.
  - A.—Occurs as a yellowish brown paper.
- S.—Feebly soluble in water, but freely soluble in presence of oxalic acid or of potassium or sodium oxalates.
  - D.—See tests for ferric salts and for oxalates.
- P.—A solution of it should not give a blue precipitate with potassium ferricyanide, and should not become turbid on boiling it with a large quantity of water.
- U.—Ferric oxalate is exceedingly sensitive to light, becoming converted into ferrous oxalate during exposure, thus  $\text{Fe}_2(\text{C}_2\text{O}_4)_3 = 2\text{FeC}_2\text{O}_4 + 2\text{CO}_2$ , and is on that account used in the platinotype process, and in certain "blue" processes. It is also employed mixed with hypo as a reducer for negatives or prints, owing to

the fact that in contact with silver it becomes converted into ferrous oxalate, silver oxalate being simultaneously formed thus,  $Ag_2 + Fe_2(C_2O_4)_3 = Ag_2C_2O_4 + 2FeC_2O_4$ , and the silver oxalate is at once attacked by the hypo, and dissolved thus,  $Ag_2C_2O_4 + 2Na_2S_2O_3 = 2AgNaS_2O_3 + Na_2C_2O_4$ .

## Ferric Sodium Oxalate.—Fe<sub>2</sub>Na<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>4</sub>

Syn., Sodio-ferric Oxalate.

C.L.—Prepared like the corresponding ammonium salt, employing sodium hydroxide to neutralise the oxalic acid.

U.—Employed in the "printing out" platinotype process.

### Ferric Sulphate.—Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>

Syn., Sulphate of Peroxide of Iron, Persulphate of Iron.

C L—Conveniently prepared by leaving a rather dilute aqueous solution of ferrous sulphate exposed to the air in an open vessel for several weeks, or by dissolving ferric oxide (colcothar, rouge, tripoli powder) to saturation in dilute sulphuric acid.

U.—Employed to clear slightly veiled gelatino-bromide negatives—a use dependent upon its slightly solvent action on metallic silver.

### Ferric Salts, Tests for.

Soluble ferric salts give the following reactions:—(1) Sodium or ammonium hydroxide produce a reddish brown precipitate. (2.) Potassium ferrocyanide produces a dark blue precipitate. (3.) Potassium ferricyanide a greenish brown colour. (4) Potassium sulphocyanate a blood red colour (5.) Ammonium sulphide a black precipitate. (6.) Sodium phosphate a reddish white precipitate.

### Ferricyanides, Tests for.

Soluble ferricyanides give the following reactions:—(1.) Ferric chloride gives a greenish brown colour. (2) Ferrous sulphate a deep blue precipitate. (3.) Silver nitrate a dark orange precipitate. (4.) Copper sulphate a greenish yellow precipitate.

## Fluorescein.— $C_6H_4[COC_6H_3(OH)_2]_2$

Syn., Resorcin-Phthalein.

 $\begin{array}{c} \text{C.L.} - \text{Made by heating resorcin with phthalic-anhydride} \\ \text{C}_6\text{H}_4(\text{OH})_2 + \text{C}_6\text{H}_4(\text{CO})_2 \\ \text{O} = \text{C}_6\text{H}_4[\text{COC}_6\text{H}_3(\text{OH})_2]_2.} \end{array}$ 

A.—Occurs as a yellowish-red powder.

S.—Feebly soluble in water, freely so in alcohol, both solutions possessing a splendid green fluorescence.

D.—Derivatives of fluorescëin yield a precipitate of this substance when heated with hydrochloric acid, and are decolorised by calcium hypochlorite.

U.—Acted upon by bromine fluorescëin yields tetrabromofluorescëin  $C_6H_4[COC_6HBr_2(OH)_2]_2$ , and this gives sodium tetrabromo-fluorescëin  $C_6H_4[COC_6HBr_2(ONa)_2]_2$ , a substance known in commerce as eosin J and yellow-shade eosin. This eosin occurs as a slightly deliquescent crystalline powder readily soluble in water and yielding solutions which fluoresce but slightly. Acted upon by iodine fluorescëin yields the corresponding sodium tetraiodo-fluorescëin known in commerce as pyrosin J or R, eosin B, erythrosin B, soluble primrose, blue-shade eosin, iodoeosin B, and dianthin B. It is a brownish-red powder, freely soluble in water to a bluish-red solution, which does not fluoresce. Both the bromo and iodo derivatives of fluorescein are employed in orthochromatic work.

### Formic Acid.-H2CO2

C L.—Prepared by distilling at 80°C two ounces of crystallised oxalic acid with 12 fluid ounces of glycerine, and condensing the fermic acid by passing the vapours through a Liebig's condenser. When six drachms have passed over, the distillation should be stopped. The change may be represented thus:  $H_2C_2O_4 = H_2CO_2$ . As the glycerine remains practically unchanged, it may be employed to prepare more formic acid by adding two ounces more oxalic acid to it and repeating the process. After some time, however, the glycerine becomes so diluted with the water of crystallisation of the oxalic acid as to considerably retard the reaction.

A.—A colourless acid liquid, having a spec. grav. of about 1.2 fuming in moist air when very concentrated, and having a pungent vinegar-like smell.

S.—Miscible with water and alcohol in all proportions.

D.—Vide tests for formates.

U.—Employed in certain collodion developers.

## Formates, Tests for.

Neutral solutions of formates give the following reactions:—(1.) Ferric chloride gives a red colour, and, on boiling the mixture, a reddish precipitate slowly forms. (2.) Silver nitrate gives in concentrated solutions a white or greyish precipitate, which darkens on boiling. No precipitate is formed if the solution is too dilute. (3.) Mercuric nitrate gives a white precipitate, which becomes grey on heating. (4.) Mercuric chloride boiled with the solution gives a slowly forming white precipitate.

### Fluorides, Tests for.

(1.) Solid fluorides heated in a test tube with strong sulphuric acid evolve hydrofluoric acid, which corrodes the sides of the tube. The corrosion is best seen after the tube has been cleaned and dried. Soluble fluorides give the following reactions:—(2.) With barium nitrate a white precipitate. (3.) With calcium chloride a white gelatinous precipitate, more manifest after the addition of ammonia.

### Ferrocyanides, Tests for.

(1.) Solid salts, heated with dilute sulphuric acid, yield prussic acid, recognisable by its almond-like smell and by the usual tests (vide Tests for Cyanides). (2.) Heated with strong sulphuric acid, they liberate carbon monoxide gas, which will burn at the mouth

of the tube with a blue flame.

Soluble ferrocyanides give the following reactions:—(3) With ferric chloride a dark blue precipitate. (4.) With ferrous sulphate a light blue precipitate, gradually deepening in tint on exposure to air. (5.) With silver nitrate a nearly white precipitate. (6.) With copper sulphate a brownish-red precipitate.

# Ferrous Ammonium Sulphate. — FeSO<sub>4</sub>(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>6H<sub>2</sub>O.

Syn., Double Sulphate of Iron and Ammonia.

- C.L.—Mix ferrous sulphate with half its weight of ammonium sulphate, and dissolve the mixture in twice its own weight of boiling water, previously acidified with sulphuric acid. On cooling crystals of the double salt will separate out.
  - A.—Occurs in pale bluish-green crystals.
- S.—Soluble in ten times its weight of cold, and twice its own weight of boiling water; nearly insoluble in alcohol.
- D.—See Tests for Ferrous Salts, Ammonium Salts, and Sulphates.
- P.—The solution should give only a faint red colour with potassium sulphocyanate, denoting absence of any considerable quantity of ferric sulphate.
- U.—Its uses are the same as those of ferrous sulphate, to which it is preferred by many workers on account of its superior stability.

## Ferrous Bromide,-FeBr<sub>2</sub>.

Syn., Bromide of Iron.

- C.L.—Take an ounce of bromine, mix it with eight ounces of water, and gradually add half an ounce of iron filings, stirring all the time with a glass rod. When the colour, at first red, changes to green, the operation is complete. Crystals of the substance may be obtained by evaporating the liquid to small bulk.
  - A.—Occurs in small green crystals.
  - S.—Fairly soluble in water, feebly soluble in alcohol.
  - D.—See Tests for Ferrous Salts and for Bromides.
  - U.—Its chief use is to prepare ammonium bromide (q.v.)

## Ferrous Iodide.-FeI2.

Syn., Iodide of Iron.

C.L.—Prepared like the bromide, taking an ounce of iodine in fine powder, and about 10z. of iron filings. Heat may be employed in this case to facilitate combination.

- A.—Occurs in small green deliquescent crystals.
- S.—Soluble in water and in alcohol.
- U.—It may be employed for iodising collodion, but its comparative instability is a drawback. It is chiefly used at present to make ammonium iodide (q.v.)

## Ferrous Nitrate.— $Fe(NO_3)_2$ .

Syn., Nitrate of Iron.

- C.L.—Prepared by dissolving an ounce of ferrous sulphate in three ounces of water, previously acidulated with a few drops of sulphuric acid, and mixing the solution with an ounce of barium nitrate, dissolved in ten ounces of water, when the following change occurs: FeSO<sub>4</sub>·7H<sub>2</sub>O + Ba(NO<sub>3</sub>)<sub>2</sub> = BaSO<sub>4</sub> + Fe(NO<sub>3</sub>)<sub>2</sub> + 7H<sub>2</sub>O. On filtering off the insoluble barium sulphate and evaporating down the liquid, ferrous nitrate will separate out.
  - A.—Occurs in confused brownish-green deliquescent crystals.
  - D.—See Tests for Ferrous Salts and for Nitrates.
- P.—Usually contaminated with much ferric nitrate evidenced by the intense red colour its solution gives with potassium sulphocyanate.
- U.—Used in collodion positive-by-reflection work (ferrotype, etc.) instead of ferrous sulphate on account of the whiter colour of the deposited silver.

# Ferrous Oxalate.—FeC<sub>2</sub>O<sub>4</sub>.

Syn., Oxalate of Iron.

- C.L.—Dissolve two ounces of ferrous sulphate in 15 ounces of water, acidified with sulphuric acid, and mix the solution with 396 grains of oxalic acid, dissolved in 15 ounces of water. After six hours or more the precipitation will be complete, when the liquid can be decanted off, and the precipitate washed and dried. The following equation represents the change:  $FeSO_4\cdot 7H_2O + H_2C_2O_4\cdot 2H_2O = FeC_2O_4 + H_2SO_4 + 9H_2O$ .
  - A.—Occurs as a pale yellow powder.
- S.—Practically insoluble in water, but freely soluble in a solution or potassium oxalate, yielding red coloured potassium ferrous oxalate  $K_2Fe(C_2O_4)_2$ .
  - D.—See Tests for Ferrous Salts and for Oxalates.
- U.—Employed as potassium ferrous oxalate (usually made as wanted by mixing solutions of ferrous sulphate and potassium oxalate) in so-called alkaline development. Assuming the developable image to consist of silver sub-bromide, its action would be represented by  $3 \text{FeC}_2 O_4 + 2 \text{Ag}_2 \text{Br} = \text{Fe}_2 (\text{C}_2 O_4)_3 + \text{FeBr}_2 + 2 \text{Ag}_2$ . If the oxybromide theory is adopted the following would possibly represent the change:  $2 \text{FeC}_2 O_4 + \text{K}_2 C_2 O_4 + \text{H}_2 O + \text{Ag}_2 O \cdot 2 \text{AgBr} = \text{Fe}_2 (\text{C}_2 O_4)_3 + 2 \text{KOH} + 2 \text{AgBr} + \text{Ag}_2$ . It must not be forgotten that prepared by mixing ferrous sulphate and potassium oxalate,

potassium sulphate, which acts as a restrainer, is introduced into the developer. To get the full developing power of ferrous oxalate, the substance itself should be dissolved in potassium oxalate.

### Ferrous Sulphate.— $FeSO_4 + 7H_2O$ .

Syn., Sulphate of Iron, Protosulphate of Iron, Green Vitriol, Copperas.

C.—Prepared commercially by the oxidation of iron pyrites, brought about by the joint agency of moisture and of atmospheric oxygen, thus,  $FeS_2 + 7O + H_2O = FeSO_4 + H_2SO_4$ . When the action is complete the product is mixed with water, and caused to act upon scrap iron, by which means the sulphuric acid it contains is utilised.

Ferrous sulphate also occurs as a bye-product in the manufacture of alum (q.v.)

L.—Dissolve one ounce of fine pianoforte wire in one and a half ounces of sulphuric acid, diluted with four ounces of water, and when solution is complete filter and evaporate down the solution. The change can be thus represented,  $Fe + H_2SO_4 = FeSO_4 + H_2$ .

A pure product may also be obtained by adding a concentrated hot aqueous solution of the commercial salt to four times its volume of rectified methylated spirit.

A.—Occurs in green crystals, which are very stable if kept dry, but rapidly oxidise if at all damp.

S.—Insoluble in alcohol, soluble in one-third of its weight of boiling, and one and a half times its weight of cold water. The aqueous solution rapidly oxidises, and various plans have been proposed to prevent this, such as covering the liquid with a layer of oil and drawing it off from the bottom as required, or preserving it in a gasogene charged with carbonic acid. The most practical plan is, however, to make the solution as required. In dissolving the salt in water it is best not to use heat or partial decomposition occurs, a basic salt being formed. It does not appear that the presence of sulphuric acid prevents oxidation, but it has the advantage of keeping the solution clear to the last. The addition of copper sulphate is said to retard oxidation.

D.—See Tests for Ferrous Salts and for Sulphates.

P.—The commercial salt almost invariably contains more or less ferric sulphate, the quantity of which may be approximately known by the colour of the crystals, these being more or less brown, particularly at the edges, when ferric sulphate is present.

U.—Ferrous sulphate is a deoxidising agent, i.e., it tends to become itself oxidised at the expense of the oxygen or its equivalent of the substance with which it is brought into contact, and its use as a wet plate developer depends upon

that fact. Thus, when ferrous sulphate is mixed with silver nitrate a precipitation of metallic silver occurs in accordance with the equation  $6AgNO_3 + 6FeSO_4 = 3Ag_2 + Fe_2(SO_4)_3 + Fe_2(NO_3)_6$ .

It is employed as such in wet plate development, mixed with silver nitrate for developing preserved collodion plates; mixed with potassium oxalate in gelatino-bromide and chloride develop-

ment, and for a variety of minor uses.

### Ferrous Salts, Tests for.

Soluble ferrous salts give the following reactions:—(1.) With sodium or ammonium hydroxides a white or nearly white precipitate rapidly changing to dirty green and finally to reddish brown. (2.) With potassium ferrocyanide a dark blue precipitate. (3.) With potassium ferricyanide a light blue precipitate, rapidly becoming dark blue. (4.) With ammonium sulphide a black precipitate.

### Galls.

### Syn., Nut Galls, Gall Nuts.

These are excrescences produced on various trees, but chiefly on oaks, by the punctures and deposited ova of the gall-fly (Diplolepis gallæ tinctoriæ.) They are collected in Cassaba, Magnesia, and other localities, and, being chiefly exported from Aleppo, are sometimes called Aleppo galls.

A.—Occurs as hard, heavy balls, about half-an-inch in diameter, and varying in colour from bluish-green (usually considered the best) to light brown.

U.—Employed in the manufacture of tannin, gallic acid, and pyrogallol.

## Gallic Acid.—C7H6O5.

C.L.—Made by exposing powdered and moistened galls to the action of the atmosphere for about three months, at the end of which the mass is subjected to considerable pressure, usually in a hydraulic press, and the pasty residue digested with boiling water, slightly acidified with sulphuric acid, the solution filtered and permitted to cool, when crystals separate out. To purify these, they are re-dissolved in water, the solution decolorised by animal charcoal, and again evaporated down.

A.—Occurs in small fawn-coloured crystals.

S.—Soluble in three times its weight of boiling, and in twenty times its weight of cold water.

D.—Ferric chloride gives a deep blue precipitate soluble in excess to a green solution, decolorised on boiling. Lime water gives a white precipitate, slowly becoming blue on exposure to air.

U.—Gallic acid was formerly used in wet-plate development, but its use has been supplanted by more energetic reducing agents. An aqueous solution of it is employed with advantage to soak gelatino-bromide plates prior to alkaline development, when the object is to obtain excessive density.

#### Gelatine.

Chemically speaking, gelatine contains carbon, hydrogen, nitrogen, oxygen, and sulphur, and is a mixture in variable proportions of two substances of indefinite composition—glutin and chondrin. Glutin in an almost pure state can be obtained by making flour into dough, tying this up in muslin, and kneading the mass under running water as long as any starch passes through. Glutin speedily putrefies when exposed moist to the air, and at 100° dries up to a brittle, horny mass. It differs from chondrin in containing no sulphur and in not being precipitated from its solutions by alum. Gelatines rich in it are specially suited for carbon printing and for photomechanical work.

Chondrin is obtained by the action of hot water on bones and cartilages. It is present in large quantities in gelatine made from bones; that made from hides containing more glutin. Chondrin, unlike glutin, is immediately precipitated by alum, and this gives a rough means of distinguishing gelatine rich in chondrin from that rich in glutin. To apply the test, make a saturated solution of chrome alum, and add it to an equal volume of a 10% hot solution of the gelatine to be tested, when, if much chondrin is present, the hot gelatine solution will stiffen to a jelly in a few seconds. Gelatine rich in chondrin appears to answer best for emulsion making.

C.—Gelatine is made commercially from two products, viz, bones and hides. It is made from the former by exposing the crushed bones to the air for several weeks, keeping them well moistened with water. The bones are then treated with hydrochloric acid, and this treatment repeated until all the calcium phosphate is dissolved out, and only a soft pulpy mass remains. This is freed from acid as completely as possible by washing it with cold water, then steeped for some time in lime water, again thoroughly washed, and finally air-dried, in which condition it will keep a long time. To prepare the gelatine the product is well softened by soaking it in water, and then dissolved, a trace of alum being added to decompose the fatty matters invariably present. After ten hours' cooking some sulphuric (or, sometimes acetic) acid is added, and the solution is then carefully filtered and permitted to set. When this occurs the jelly is cut into thin sheets or strips, and airdried.

Another process consists in treating crushed bones with phosphoric acid, which dissolves out the calcium phosphate, the residue being then treated as above. A current of sulphur dioxide is passed through the solution of acid calcium phosphate, obtained as a bye-product, when calcium sulphite is precipitated, and is converted into sodium sulphite by mixing it with sodium carbonate. The phosphoric acid left in solution after the sulphur dioxide has been passed through the acid calcium phosphate is merely diluted with water and used over again, and so the process becomes a continuous one, so far as phosphoric acid is concerned.

Gelatine made from bones is usually acid, this being derived from residual traces of the acids employed in its manufacture. Calcium carbonate, alum, and iron are also present in small quantities. The bones of oxen are preferred by gelatine makers, as those of sheep, calves and hogs yield a jelly which obstinately retains a brown colour, and smells of tallow.

In making gelatine from hides only the "roundings" or portions from the cheeks and neck are, as a rule, used. These are useless for leather making, and yield a product of better quality than the larger pieces. The hides are first treated with lime, alum, and water to remove the blood and hair, and to open the pores of the skin. The treatment consists in placing alternate layers of the mixture and of the skins in deep pits, in which they remain for about six months. At the expiration of this time the skins are washed until every trace of lime and alum has been got rid of, and then hung up to dry. In this condition the material keeps for an almost indefinite period. To prepare the gelatine the purified skins are steeped in water until perfectly soft, and then cut up into minute shreds. These are then placed in warm water and kept at as low a temperature as is consistent with the solution of the skins. When the whole is melted the liquid is filtered through animal charcoal, permitted to set, and then sliced up and dried.

Gelatine prepared from hides is generally neutral or slightly alkaline, and contains, as a rule, neither alum nor lime.

Gelatine is in many respects like glue, which is made in a similar way, employing the refuse and parings of hides and skins of every description. Bonnet glue is a pure variety of glue used by milliners, and is of much better quality than many foreign samples of gelatine.

To purify a bad sample of gelatine the following process answers:

—Cut it up into as small pieces as possible, and soak for 24 hours in a large quantity of repeatedly renewed distilled water. Finally, dissolve the whole at as low a temperature as possible in about 20 times its weight of distilled water; acidify the solution, if not already acid, with acetic acid, and mix intimately with white of egg beaten to a froth, using the white of one egg for every pint of solution. Next heat the mixture to boiling as rapidly as possible, and then permit the whole to remain at rest for some time, when the coagulated albumin will rise to the top, carrying suspended matters, fat, and alum with it. When the whole has set, the upper portion containing the coagulated albumin is cut off, the clear residue melted, squeezed through canvas into distilled water, washed thrice with distilled water, steeped in strong alcohol for a few hours to get rid of the water, and finally air-dried.

A.—Gelatine occurs in sheets or shreds, that made in France being, as a rule, whiter than English or German products. This appears to be due to the fact that many large French manufacturers employ fish bones in its manufacture. Airdried gelatine contains from 5 to 20% of water, which it gives up only at 120° or 130°C.

Gelatines are classified photographically as hard, medium and soft, according to the hardness or the reverse of a solution of given strength, as tested by the crushing force required to break the jelly it forms on cooling. Roughly speaking, this hardness varies inversely as the weight of water which the sample will absorb. As a rule, gelatine which swells easily and rapidly is soft and soluble at a low temperature, whilst hard gelatine swells slowly and requires a higher temperature to melt it.

S.—Placed in water at about 15°C., gelatine swells out to five or six times its original volume, and dissolves completely when heated to from 30° to 40°C. Oxalic, acetic, hydrochloric and sulphuric acids dissolve gelatine in the cold.

D.—Dry gelatine strongly heated in a tube does not fuse, but swells up and decomposes, yielding offensive-smelling alkaline vapours. A fairly concentrated aqueous solution gives the following reactions: (1) Strong alcohol gives a flaky whitish precipitate; (2) tannin a greyish white precipitate; (3) mercuric chloride a white precipitate.

P.—Good photographic gelatine should be nearly colourless, should absorb at least six times its own volume of water at 15°C., and dissolve easily and completely on heating the mixture to 30° or 40°C. Its aqueous solution should become solid on standing, even when containing only 1% of gelatine, and should not putrefy on standing for 24 hours. When icinerated the ash should not exceed 3% of the whole. The greater the crushing force the sample will bear, the better it is considered to be, the test, really a comparative one, being carried out as follows: A given weight of the sample to be tested, and the same weight of another well-known brand used as a standard, are separately swelled and then dissolved in equal volumes of water. The jellies are then permitted to set in two vessels of the same shape and size, and after ten hours or more a small metal tray is placed on the surface of each, and this is loaded with weights until the jelly gives way.

Fracture is a rough practical test of the quality of gelatine, the poorer varieties being brittle and breaking short like glass, the better kinds being tough and having a horny fracture.

U.—The properties which render gelatine valuable from a photographic standpoint are—(1) Its insolubility in cold water; (2) its solubility in hot water; (3) the fact that it is rendered insoluble when mixed with certain substances like potassium dichromate, and then exposed to light; (4) the fact that it is rendered insoluble by other substances such as chrome alum without previous exposure to light.

These properties render it available for emulsion making, in which the viscous gelatine keeps the comparatively heavy silver haloids in suspension; in carbon printing and photo-mechanical work, in which the pigmented or plain tissue under the different parts of the negative is rendered insoluble in proportion to the intensity of the light and to its duration.

The use to which the gelatine is to be put determines whether it shall be soft, hard, or medium. Hard gelatine is, as a rule, preferred for photo-mechanical processes. Medium and soft for carbon printing and emulsion making. Very soft gelatine used for emulsions gives a fine even film, but frills too readily to be of practical use, although this can be compensated for to a great extent by the judicious use of chrome alum. It will be inferred from this that the presence of traces of alum in gelatine is not prejudicial to its employment in emulsion making.

Gelatine, particularly if very soft, undergoes decomposition when repeatedly heated or when maintained for a long time in the liquid state. The change is manifested by its refusing to solidify on cooling, and is probably caused by the chondrin it contains combining with the water present to form a definite hydrate. It is for this reason that in emulsion making the bulk of the gelatine is usually added after emulsification is complete. The same change is brought about by acetic and nitric acids, and zinc chloride, which, even when present in small quantities, prevent solutions of gelatine from setting at all.

Phenol (carbolic acid), salicylic acid, chloral hydrate and glycerine retard, on the other hand, the decomposition, and the latter is for that reason frequently directed to be used in emulsions made by the boiling process.

As regards the employment of gelatine for processes other than emulsion making, potassium dichromate soon renders damp gelatine insoluble, even in the dark, hence the recommendation to dry carbon tissue as quickly as possible, and to preserve it in a dry place. It is interesting to note in this connection that a damp mixture of potassium dichromate and gelatine is practi-

cally insensitive to light.

Dry gelatine mixed with potassium dichromate and exposed to light is thereby rendered insoluble, and the use of such a mixture in carbon printing, Woodburytype, photo-zincography, etc., depends upon this fact. The principle is also utilised in preparing an insoluble and thin support for sensitive emulsions. To do this, a thin film of gelatine, mixed with dichromate, is exposed to the light until brown, and then decolorised with sulphurous acid. Such a film (Vergara tissue) is very tough, nearly transparent, very thin and light, and insoluble in water, but it possesses the disadvantage of absorbing water, and consequently swells out very considerably when immersed in that liquid.

As has been previously pointed out, gelatine swells out when placed in water, and the higher the temperature of the liquid up to about 15°C. the greater the amount of water absorbed. For this reason the employment of as cold a sensitising solution as possible is recommended in sensitising carbon and other tissues. Swelled gelatine, from which the excess of liquid has been squeezed out, melts at a much higher temperature than the same gelatine in presence of an excess of water, on which account it is advisable to remove the excess of sensitising solution from moist

carbon tissue by squeegeeing it on a glass plate.

# Glycerine.—C<sub>3</sub>H<sub>5</sub>(OH)<sub>3</sub>.

Syn, Glycerol, Propenyl Alcohol.

C.—Prepared on a large scale by decomposing palm oil by means of steam heated to 315°C. Palm oil is, chemically speaking, propenyl palmitate, and is decomposed at a high temperature in contact with water into glycerine, which dissolves in the water and palmitic acid, which floats as an oily layer on the top. The change is represented by the equation  $C_3H_5(C_{16}H_{31}O_2)_3 + 3H_2O = C_3H_5(OH)_3 + 3HC_{16}H_{31}O_2$ . At the conclusion of the process the palmitic acid is skimmed off and employed for making candles, and the mixture of glycerine and water evaporated down until it reaches a spec grav. of 1·15, when steam, at ordinary pressure, is passed through it until the condensed water ceases to have an acid reaction. The temperature of the steam is then raised to 180°C., and the distillate passed through a receiver kept at a temperature of about 110°C., by which means the glycerine only is condensed in a practically anhydrous condition.

Glycerine also occurs in the refuse liquors of soap makers, from which it is extracted by concentrating the liquid and mixing the residue with alcohol, which dissolves out the glycerine. On distilling the mixture the alcohol passes over and is condensed, the

glycerine remaining behind.

L.—To prepare glycerine on a small scale, a mixture of olive oil (propenyl oleate) and water is boiled with an excess of litharge (lead oxide), when an insoluble residue of lead oleate (the emplastrum plumbi of the druggist) remains, and glycerine passes into solution, thus,  $2C_3H_5(C_{18}H_{33}O_2)_3 + 3PbO + 3H_2O = 3Pb(C_{18}H_{33}O_2)_2 + 2C_3H_5(OH)_3$ . After filtration, sulphuretted hydrogen is passed through the liquid to remove the lead oleate in solution, the liquid again filtered and finally concentrated by evaporation.

Glycerine decomposes if it is attempted to distil it in the ordinary way, but can be easily redistilled in presence of steam

heated to about 180°C.

A.—Occurs as a clear, colourless, thick liquid with a sweet taste, which should possess a spec. grav. of 1.23.

S.—Miscible in all proportions with water and alcohol.

D.—Heated with concentrated sulphuric acid it blackens and yields acrolein, recognisable by its penetrating smell of burning fat. Heated with phenol (carbolic acid) and a little sulphuric acid it yields a mass soluble to a magnificent red in dilute ammonia.

P.—If the spec. grav. is considerably below 1.23, the sample is probably diluted with water, and provided other matters are absent it is easy to ascertain the quantity of water present from the specific gravity of the sample. For this purpose the following formula is generally used:—

 $P = \frac{1266 - 1000d}{2.66d}$ 

in which d is the spec. grav. of the sample as compared with water at 15°C., and P the percentage of glycerine actually present.

Glucose and cane sugar are often used to adulterate glycerine; and lead and calcium salts, and oxalic and formic acids are met with as the result of imperfect purification. To detect glucose, boil the sample with an excess of caustic soda and a drop or two of copper sulphate, when if glucose is present a red precipitate will be produced.

Cane sugar is detected by boiling the diluted sample for twenty minutes with a little sulphuric acid, and then applying the glucose test, the sulphuric acid converting any cane sugar present into glucose. A simpler plan is to evaporate the diluted sample with a few drops of sulphuric acid at 100°C., when blackening will occur if cane sugar is present.

Lead and calcium are best identified by burning the glycerine in an evaporating dish, dissolving the residue in the smallest possible quantity of nitric acid, diluting this solution with water into two parts, and passing sulphurreted hydrogen into one, when a black precipitate will indicate lead, and adding ammonium oxalate to the other, when a white precipitate will indicate calcium.

Formic acid is detected by the blackening which occurs on warming the diluted sample with ammonio-nitrate of silver, and oxalic acid by the white precipitate it yields with calcium acetate.

U.—Glycerine is an antiseptic, and its use in photography depends upon this fact. It is employed to preserve solutions of pyrogallol and other perishable substances, and in emulsion making to retard the decomposition of the gelatine (q.v.)

#### Gold.-Au.

C.—A metal occurring as such, mixed with sand or quartz, in various parts of the world, the main supplies being obtained from Australia, Africa, and Austria. From auriferous sands the precious metal is extracted by washing the mixture in a cradle or inclined wooden trough furnished with rockers, and having an opening at one end for the escape of the water. The sand is thrown on a grating at the head of the cradle, and this retains the larger stones, whilst the sand and gold pass through, the sand in virtue of its lighter spec. grav. (2.6) being washed away through the opening, whilst the heavier gold (spec. grav. 19.4) is retained, and is found at the conclusion of the process at the bottom.

From auriferous quartz the gold is extracted by crushing the rock, and then washing the crushed mass with water, or by fusing the quartz with litharge, charcoal, and lime, by which means the lead is reduced, and alloys itself with the gold, the alloy sinking to the bottom, whilst the lime forms with the quartz a fusible slag of calcium silicate, which floats on the top. The gold prepared by the latter process is freed from lead by heating the alloy on the bed of a reverberatory furnace coated with bone-ash, when the lead oxidises, and the litharge so formed fuses, and is absorbed by the porous bed of the porous furnace bed (vide Lead). Other more complicated processes are adopted when the gold occurs mixed with iron, copper, or silver.

A.—Pure gold is a yellow, soft metal, unfit, on account of its softness, for either coinage or jewellery. For these latter purposes it is hardened by being alloyed with copper. English gold coin contains  $\frac{1}{12}$ ths of pure gold, and  $\frac{1}{12}$ th of copper, whilst jewellery usually contains from  $\frac{1}{12}$ th or less to  $\frac{1}{12}$ ths of gold. In Australia silver is employed in place of copper to harden gold coin, and Australian gold coins are for that reason somewhat lighter in colour than English ones. The degree of purity of gold is expressed in carats, i.e., in the quantity of gold contained in 24 parts by weight of the alloy. Thus pure gold is said to be 24 carats, English coinage 22 carats, Australian coinage 21.6 carats, and jewellery from 8 to 18 carats fine. The gold "Hall mark" is the same as the silver one (q.v.) The "Standard mark" is for gold of the same standard as sterling silver, also the same as the latter. Gold 18 carats fine is marked with a crown and a figure of 18. Gold of lower standard carries no mark.

L.—To obtain pure gold from gold coin, &c., dissolve it preferably on the water bath in hydrochloric mixed with one-fourth of its volume of nitric acid, and evaporate the solution nearly to dryness. Next dilute it with a considerable volume of water (say an ounce for every five grains of coin, &c., originally taken), filter the liquid and mix it with a saturated solution of ferrous sulphate containing eight times as much salt as of coin, &c. This will precipitate the gold as a dark purple powder, which should be collected on a filter well washed with boiling dilute hydrochloric until the washings cease to colour potassium ferrocyanide, and then re-dissolved in aqua regia and evaporated to dryness at 100°C. If the solution is not evaporated to dryness in the first instance, some of the gold will escape precipitation with the ferrous sulphate, and if hot water is employed instead of hydrochloric acid to wash the precipitated gold, it will be found that the final product will contain iron. The action of the ferrous sulphate upon the gold trichloride (AuCl<sub>3</sub>) is represented by the following equation:  $2AuCl_3 + 6FeSO_4 = Au_2 + Fe_2Cl_6 +$ 2Fe<sub>2</sub> (SO<sub>4</sub>)<sub>3</sub>. Oxalic acid is frequently employed instead of ferrous sulphate to precipitate the gold, in which case the weight of oxalic acid should be three times as great as that of the gold, and the mixed solutions should be boiled for some time to insure complete precipitation. The following equation represents the action of the oxalic acid:  $3H_2C_2O_4 + 2AuCl_3 = 6HCl + Au_2 + 6CO_2$ . When oxalic is used it is unnecessary to wash the precipitated gold with hydrochloric acid, as hot water will get rid of everything soluble.

When extracting pure gold from jewellery, etc., of poor quality, it is best to first file or granulate it, and then boil the powder for sometime with strong nitric acid before attempting to dissolve it in aqua regia. This will dissolve out most of the silver (sometimes present in considerable quantity), and so render subsequent solution easier, as when the greater part of the silver is not first removed in this way a layer of silver chloride is apt to form on the surface of

the crude gold, and stop, or at all events retard very considerably, the action of the mixed acids.

If gold lace is being utilised, it is best to begin by heating it to redness, so as to remove the cotton, etc., and then treat it as above.

D.—Gold dissolved in aqua regia will give the reactions mentioned under salts of gold (q.v.)

S.—Insoluble in any single acid but selenic, but soluble in chlorine or bromine water, and in aqua regia.

U.—Employed to manufacture gold trichloride.

The following table, due to Mr. Thos. Fletcher, of Warrington's shows the composition of the commoner gold coins.

### GOLD COINS.

Country.	Name of Coin.	Fineness.		Standard Weight of Coin.	Weight of Pure Gold.	Value.
England France United States India Austria Prussia	Sovereign Napoleon Eagle Mohur Ducat Frederick (1800)	Crts. 22 21 21 22 22 23 21	Grs. 0 21 4 32 0 23 2	123 <sup>1</sup> / <sub>4</sub> 97 <sup>1</sup> / <sub>2</sub> 268 <sup>1</sup> / <sub>2</sub> 180 58 <sup>1</sup> / <sub>6</sub> 100 <sup>1</sup> / <sub>2</sub>	113 89½ 246 165 53⅓ 92¼	s. d. 20 0 15 10 43 6 <sup>1</sup> / <sub>2</sub> 29 2 <sup>1</sup> / <sub>2</sub> 9 5 <sup>1</sup> / <sub>4</sub> 16 4

## Gold Trichloride. $-AuCl_3 + 2H_2O$ .

Syn., Auric Chloride, Chloride of Gold.

C.L.—Prepared by dissolving gold in hydrochloric, mixed with one-fourth cf its volume of nitric acid (aqua regia), and evaporating down to small bulk, or, if crystals are not required, merely evaporating to dryness, the evaporation being effected on the water bath to avoid spirting and loss of precious metal. The following equation represents the change: 3HNO<sub>3</sub> + 9HCl + Au<sub>2</sub> = 2AuCl<sub>3</sub> + 6H<sub>2</sub>O + 3NOCl, from which it will be seen that about three ounces of the mixed acids are requisite for every ounce of gold. Practically four ounces of mixed acids are employed for every ounce of precious metals, and this proportion will be found a satisfactory one to adopt. Of course, a large excess of mixed acids means loss of material in the shape of the acids evaporated off, to say nothing of the loss of time and cost of fuel, &c., in doing this.

In practice many photographers prepare their own gold chloride by dissolving gold coin in aqua regia, using as little acid as possible, and then merely neutralise the solution as required with chalk. It does not appear that the copper which is present, or the calcium chloride formed by the addition of the chalk, exert any influence on the final result. A very simple calculation will show that there is a considerable saving in making gold chloride from coin.

- A.—Deposited from solutions containing an excess of acid gold chloride occurs in yellow crystals represented by the formula  $\mathrm{AuCl_3}\cdot\mathrm{HCl}\cdot\mathrm{4H_2O}$ , but by carefully heating these crystals they become converted into a reddish brown semi-crystalline mass represented by the formula  $\mathrm{AuCl_3}\cdot\mathrm{2H_2O}$ . Both varieties of gold chloride are extremely deliquescent.
- S.—Freely soluble in water to a yellowish solution. Feebly soluble in alcohol.
- U.—Almost every substance capable of combining with oxygen or with chlorine tends to reduce the metal from a solution of gold chloride, and the operation of toning depends upon this fact. The precipitation of gold occurs most readily in alkaline solutions, and least readily in acid ones.

Soluble salts of feeble acids, such as the alkaline or earthy carbonates, hypochlorites, borates, phosphates and acetates, mixed with gold chloride, constitute the chief toning bath for silver prints. The rapidity with which the gold is deposited appears in great measure to influence its colour. When slowly deposited it is thrown down as a reddish powder, when rapidly deposited as a bluish-black one.

The action of the chief toning solutions is represented by the following equations, assuming in each case that the darkened silver reduction product consists of silver oxychloride (Ag<sub>2</sub>O· 2AgCl).

- 1. Sodium acetate—15(Ag<sub>2</sub>O· 2AgCl) + 2AuCl<sub>3</sub> + 6NaH<sub>3</sub>C<sub>2</sub> = Acetic acid.
- $6\text{NaClO}_3 + \text{Au}_2 + 15\text{Ag}_2 + 30\text{AgCl} + 6\text{H}_4\text{C}_2\text{O}_2.$ 
  - 2. Calcium by pochlorite —  ${\rm Ag_2O \cdot 2AgCl} + {\rm 2AuCl_3} + {\rm 3H_2O} + {\rm Calcium}$  chlorate.
- CaCl<sub>2</sub>O<sub>2</sub> = Ca (ClO<sub>3</sub>)<sub>2</sub> + Au<sub>2</sub> + Ag<sub>2</sub> + 2AgCl + 6HCl.
- $3\text{Na}_2\text{B}_4\text{O}_7 = 6\text{NaClO}_3 + \text{Au}_2 + 15\text{Ag}_2 + 30\text{AgCl} + 12\text{H}_3\text{BO}_3.$ 
  - 4. Sodium carbonate— $15(Ag_2O \cdot 2AgCl) + 2AuCl_3 + 3H_2O + Carbonic acid.$
- $3\text{Na}_2\text{CO}_3 = 6\text{NaClO}_3 + \text{Au}_2 + 15\text{Ag}_2 + 30\text{AgCl} + 3\text{H}_2\text{CO}_3.$
- 5. Sodium phosphate  $-15(Ag_2O \cdot 2AgCl) + 2AuCl_3 + 3H_2O + Phosphoric acid.$  $3Na_2HPO_4 = 6NaClO_3 + Au_2 + 15Ag_2 + 30AgCl + 3H_3PO_4.$

## Gold Sodio-chloride.—AuCl<sub>3</sub> NaCl 2H<sub>2</sub>O.

Syn., Chloride of Sodium and Gold.

- C.L.—Made by mixing five parts by weight of gold chloride and one part by weight of pure sodium chloride, dissolving the mixture in the smallest possible quantity of boiling water, and permitting the solution to cool, when the double salt will crystallise out.
- A.—Occurs in deep yellow elongated prisms, which are permanent in fairly dry air.
  - S.—Freely soluble in water, almost insoluble in alcohol.

D.—See Tests for Salts of Gold and Sodium.

U.—Similar to those of gold chloride (q.v.) It is the form in which the so-called gold chloride is almost invariably retailed.

### Gold, Tests for Salts of.

Solutions containing gold give the following reactions:—(1) With sulphuretted hydrogen, a blackish-brown precipitate; (2) with ammonium hydroxide, a reddish-yellow precipitate, provided the gold solution be sufficiently concentrated; (3) with ferrous sulphate or oxalic acid, a brownish precipitate of metallic gold; (4) with stannous chloride mixed with a little chlorine water, a brownish-purple precipitate (purple of Cassius).

### Gum Arabic.

Syn., Gum Acacia.

Although called gum arabic, little or none of this substance comes from Arabia, the chief sources of supply being Turkey, Senegal, India, and the Cape. The best variety is known as picked Turkey and gum Senegal. It is the dried natural exudation of the trunk and branches of various species of acacia.

- A.—Occurs in nearly round tears or in fragments which vary in colour from dark brown to faint yellow, the better varieties being almost colourless.
  - S.—Freely soluble in water, insoluble in alcohol.
- U.—Employed in photography in the powder process, and in photo-lithography. Its use in these processes depends upon the fact that, like gelatine, its solubility in water is decreased by exposure to light mixed with potassium dichromate. It is also employed for mounting prints. A little salicylic acid will preserve gum arabic mucilage for a long time, and the addition of aluminium sulphate, or, in a lesser degree, of alum, greatly increases its adhesiveness.

### Gum Elemi.

The gummy exudation of the canarium commune, imported from the Phillipine Islands and the Mauritius.

- A.—A soft resin of granular consistence, somewhat resembling old honey, colourless when pure, but generally grey or brown from the presence of carbonaceous matters. It has a strong lemon-like odour, and hardens and becomes yellow on exposure to air.
  - S.—Freely soluble in alcohol.
- U.—Employed in the preparation of photographic varnishes, as it reduces the brittleness of other gums, although too soft to be used alone.

### Hydrobromic Acid.—HBr.

- C.L.—This substance, which is really a solution of gaseous hydrobromic acid in water, can be prepared by any of the following methods:—
- (1.) In a 40oz. glass retort place 1oz. amorphous phosphorus and 10oz. water. Having immersed the retort in ice-cold water,

add in small quantities at a time 3oz of liquid bromine, shaking the vessel after each addition. By operating thus the bromine and phosphorus first combine to form phosphorus tribromide, in accordance with the equation,  $P + Br_3 = PBr_3$ , and this in contact with water is split up into phosphorus acid and hydrobromic acid, thus,  $PBr_3 + 3H_2O = H_3PO_3 + 3HBr$ .

When all the bromine has been added the retort is connected by means of a tube bent at right angles, with a 20oz. bottle containing 5oz. of distilled water, and the contents distilled until the liquid in the retort has been reduced to one-quarter of its original bulk, the bent tube connected with the retort being caused to dip beneath the surface of the water in the bottle. By this means the gaseous hydrobromic acid and a good deal of the water distil over, and are condensed in the bottle. If the acid so obtained is not colourless, it may be rendered so by being agitated with a little mercury, which will combine with the free bromine present to form mercurous bromide. After standing for a couple of hours the colourless acid may be decanted off.

- (2.) When sulphuretted hydrogen is passed through bromine water sulphur is deposited and hydrobromic acid formed in accordance with the equation  ${\rm Br_2} + {\rm H_2S} = {\rm S} + 2{\rm HBr}$ . As bromine is not very soluble in water the acid obtained in this way will be rather weak, but a strong acid may be obtained by mixing equal volumes of carbon disulphede and bromine, covering the liquid with twice its volume of water, and passing sulphuretted hydrogen gas through it, taking care to lead the tube conveying the sulphuretted hydrogen to the bottom of the heavy carbon disulphide and bromine. By this means the hydrobromic acid dissolves in the water, and the liberated sulphur is taken up by the carbon disulphide. When the latter is decolorised the process is at an end.
- (3.) By mixing bromine and powdered sulphur together bromine disulphide Br<sub>2</sub>S<sub>2</sub> is formed, and this, in contact with water, yields hydrobromic acid and other products. To make use of this reaction one ounce of finely-powdered stick sulphur is placed in a 40oz. flask and covered with eight measured ounces of liquid When combination has occurred, the heavy oilylooking liquid which results is slowly poured into lukewarm water, when it decomposes into sulphuretted hydrogen, sulphurous acid, and hydrobromic acid, thus,  $Br_2S_2 + 3H_2O = H_2S +$ 2HBr + H<sub>2</sub>SO<sub>3</sub>. A strong solution of barium hydroxide is next added to the liquid as long as a precipitate (barium sulphite) falls, and the whole exposed to strong light for several weeks. By this means the sulphuretted hydrogen is decomposed into water and sulphur, which is slowly precipitated, and the liquid on being filtered contains hydrobromic acid. The completion of the reaction is known by the liquid ceasing to give a black precipitate with lead nitrate.
- (4.) A very simple method of preparing a dilute solution of hydrobromic acid consists in exposing bromine water to strong sunlight until colourless.

A.—Hydrobromic acid is a nearly colourless liquid, which, unless saturated at 0°C., fumes but slightly in air. Being heavier than water the quantity of actual hydrobromic acid in commercial samples can be ascertained approximately from their specific gravities, the following table being employed for that purpose:—

Spec. grav. at 15°.	Percentage of pure hydrobromic acid.	T.
1.08	10.4	
1.190	23.5	
1.248	30.0	
1.385	40.8	
1.475	48.5	
1.515	49.8	

#### D.—See Tests for Bromides.

P.—Is usually quite pure, but, of course, the actual quantity of hydrobromic acid present will vary in different samples. Occasionally iodine is met with in hydrobromic acid, and may be detected by adding starch paste and a trace of bromine or chlorine water to it, when, if iodine is present, a blue colour will be produced. A sample of hydrobromic acid containing iodine may be perfectly freed from that substance by being redistilled over potassium bromide.

U.—Employed in photography to make certain bromides.

### Hydrochloric Acid -HCl.

Syn., Muriatic Acid, Spirits of Salt.

This, like the preceding, is actually a solution of hydrochloric acid gas in water.

C—Occurs as a bye-product in the manufacture of sodium carbonate (q.v.)

L.—Pure hydrochloric acid may be obtained thus:—In a 30oz. tubulated retort, the slightly upturned neck of which is connected with a wide glass tube bent at an acute angle, place 4oz. of perfeetly dry white table salt, and pour over this by means of a thistle funnel, introduced through the tubulure, a cold mixture of 70z. strong sulphuric acid, and 2oz. of water. Having placed 6oz. of distilled water in a bottle, itself surrounded by cold water containing, if possible, some ice, arrange the end of the tube so that it dips not more than 1 th of an inch below the surface of the water. On heating the retort hydrochloric acid gas will be steadily evolved, and will condense in the water, which will gradually increase in volume. When the 6oz. of water have become 8oz. the operation is at an end. The change is represented thus,  $H_2SO_4 + NaCl = NaHSO_4 + HCl$ , the hydro-potassium sulphate remaining behind in the retort. At the conclusion of the operation this should be poured out into an evaporating dish whilst still liquid and hot, as if permitted to cool and solidify its removal will probably result in the fracture of the retort.

S

A.—Pure hydrochloric acid is a nearly colourless, strongly acid liquid, fuming strongly in air when a bottle of it is opened. The spec. gravity of a sample affords an easy and sufficiently accurate way of ascertaining its actual strength. The following table exhibits the spec. gravities of acids of different degrees of concentration:—

	Percentage of pure hydro-
spec. grav. at 15°.	chloric acid present.
1.0103	$2 \cdot 22$
1.0189	3.80
1.0310	$6\cdot 26$
1.0557	11.02
1.0751	15.20
1.0942	18.67
1.1048	20.91
1.1196	23.72
1.1308	25.96
1.1504	29.72
1.1588	31.50
1.1730	34.24
1.1844	36.63
1.1938	38.67
1.2021	40 51
1 2074	41.72
1.2124	43.09

D.—See Tests for Chlorides.

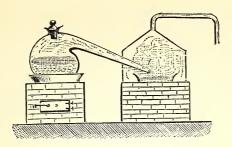
P.—Hydrochloric acid diluted with six times its volume of water should give no precipitate with barium nitrate, denoting absence of sulphuric acid. The commercial crude acid usually contains iron (as evidenced by the red colour it gives with potassium sulphocyanate) and organic matter. Free chlorine is also frequently present, and is tested for by adding a drop or two of the acid to a mixture of starch paste and potassium iodide, when if free chlorine is present a blue colour will be produced.

U.—Employed in photography to prepare certain chlorides, and for a variety of minor uses, such as dissolving out ferric oxalate from platinotype prints, etc. For these purposes only the "pure" acid should be employed.

### Hydrofluoric Acid.—HF.

Properly speaking this is a gas, but the name is given in commerce to the solution of that gas in water.

C.—Prepared commercially by acting upon finely-powdered calcium fluoride (fluor spar) with sulphuric acid and condensing the liberated gas in water. As it attacks glass the operation is carried out in vessels of platinum or of lead arranged as shown in the accompanying figure. The action of the sulphuric acid upon the calcium fluoride is represented thus,  $\rm H_2SO_4 + \rm CaF_2 = \rm CaSO_4 + \rm 2HF$ . Guttapercha bottles are employed to store the acid, or, failing these, glass bottles coated internally with beeswax.



A.—A strongly acid corrosive liquid etching glass, and forming

dangerous sores when brought in contact with the skin.

U.—Employed in photography to strip gelatine films from glass and to etch glass in various photo-mechanical processes. The liquid acid etches glass bright, whilst the gaseous acid etches it matt. Its action upon glass depends upon the fact that glass is a complex silicate, and that all silicates are attacked by hydrofluoric acid, silicon tetrafluoride (SiF<sub>4</sub>) being formed. As porcelain is like glass, a complex silicate, dishes made of this material cannot be employed with this acid. If, however, porcelain or glass dishes are coated with paraffin, or better still with beeswax, they can be rafely used when the acid is so dilute as to no longer fume. Guttapercha dishes may be used with even the strongest acid.

## Hydrogen Peroxide.-H2O2.

Syn., Peroxide of Hydrogen, Hydrogen Dioxide, Hydroxyl.

C.L.—To prepare pure hydrogen peroxide, the first step is to purify commercial barium peroxide. This is effected as follows:-The finely powdered substance is added in small quantities at a time to pure hydrochloric acid, diluted with three times its volume of water, until the acid is nearly, but not quite, neutralised, and the solution so obtained is mixed with one-eightieth of its bulk of a saturated solution of barium hydrate (Ba(OH)<sub>2</sub>), and filtered from the iron and calcium, which will be precipitated. The filtrate is then mixed with barium hydrate solution so long as a precipitate continues to form, and this precipitate, which is pure barium peroxide, is collected on a filter, well washed with cold water, and preserved in a moist condition in a stoppered bottle. To prepare hydrogen peroxide, a mixture of one volume of strong sulphuric acid and six volumes of water is cooled to 0° C. by being placed in broken ice, and the moist barium peroxide is added to it in small quantities at a time until the acid is exactly neutralised. After standing for a couple of hours, the liquid is filtered, and contains 5 % of hydrogen peroxide, and is of sufficient strength for most purposes. The action of the sulphuric acid upon the barium peroxide is represented thus,  $BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2$ . The liquid should be kept in a cool dark place and in a well-stoppered bottle.

A.—A colourless, neutral, or faintly acid liquid, possessing a peculiar metallic taste, and liberating oxygen on being gently warmed. Commercial hydrogen peroxide is usually sold as "10 volume," meaning that any volume of it is equivalent in oxidising power to ten times that volume of oxygen. This would correspond to a strength of about 3 %.

U.—Being an energetic oxidising agent, it has been proposed as a hypo eliminator, which it effects by converting any residue of sodium thiosulphate into a salt of one or more of the higher sulphur acids.

It is also a valuable test for iodides in presence of chlorides or bromides, as it liberates iodine from its metallic compounds, whilst it is without action upon chlorides or bromides.

### Hydroxylamine Hydrochloride,—NOH3HCl.

Syn., Oxyammonium Chloride.

C.L.—Either of the following processes will yield a pure product, the latter one being, perhaps, the easier to carry out:—(1.) In a Winchester quart bottle place 12oz. of ethylic nitrate, 40oz. of granulated tin, 100oz. of strong hydrochoric acid, and 300oz. of water, and let the materials remain in contact with each other for three days, shaking the bottle from time to time, when, in accordance with the equation,  $C_2H_5NO_3 + 3SnCl_2 + 6HCl = NOH_3 + C_2H_5OH + H_2O +$ 3SnCl<sub>4</sub>, hydroxylamine, ethylic alcohol, water, and stannic chloride will be formed. When the action is complete decant off the liquid, dilute it with three times its volume of water, and pass in sulphuretted hydrogen, so long as a yellow precipitate forms. By this means the stannic chloride is converted into stannic sulphide thus,  $SnCl_4 + 2H_2S = SnS_2 + 4HCl$ , and the hydrochloric acid set free combines with the hydroxylamine to form hydroxylamine hydrochloride. The liquid is next filtered, evaporated down to small bulk, when the alcohol escapes as vapour, and on cooling crystals of hydroxylamine hydrochloride, mixed with ammonium chloride and traces of tin chloride, separate out. To purify these they are first washed with strong alcohol to get rid of the tin salts, then redissolved in the smallest possible quantity of water; the solution, mixed with excess of chloro-platinic acid, permitted to stand for twenty-four hours, and the liquid decanted off from the insoluble ammonium chloroplatinate and evaporated down to small bulk.

(2.) In a Winchester quart mix 2½oz. by weight of pure metallic mercury with twenty fluid ounces of strong nitric acid (spec. grav. 1·42), previously diluted with ten ounces of water, and put the bottle in a warm place until the mercury dissolves. Meanwhile, make a mixture of 33oz. of redistilled methylated spirit and 3oz. of water, and add 18oz. of this to the mercury solution, and when ebullition ceases add the remainder, and let the whole stand over night. Next day decant off the liquid from

the precipitated mercury fulminate, and wash the latter twice by decantation. Next transfer the moist precipitate to a porcelain dish, drain off as much water as possible, dissolve it in  $2\frac{1}{2}$  ounces of strong pure hydrochloric acid (spec. grav. 1·17), and evaporate the whole down to  $\frac{1}{3}$  of its bulk. Then dilute the liquid with 10 ounces of water, and pass in sulphuretted hydrogen as long as a precipitate forms; filter this off, and evaporate the whole to dryness at  $100^{\circ}$ C. The reactions involved in this process are represented by the following equations:—

a.—Action of nitric acid upon mercury:—

$$8HNO_3 + 3Hg = 3Hg(NO_3)_2 + 4H_2O + 2NO.$$

b.—Action of nitrous acid (formed by reaction between alcohol and excess of nitric acid) and alcohol upon mercuric nitrate:—

2HNO<sub>2</sub> + C<sub>2</sub>H<sub>5</sub>OH + Hg(NO<sub>3</sub>)<sub>2</sub> = HgO<sub>2</sub>(CN)<sub>2</sub> + 3H<sub>2</sub>O + 2HNO<sub>3</sub>. c.—Action of hydrochloric acid upon mercuric fulminate:—

Formic acid.

$$HgO_2(CN)_2 + 2HCl + 4H_2O = 2H_2CO_2 + 2NOH_3 + HgCl_2$$

d.—Action of sulphuretted hydrogen to precipitate mercury as sulphide:—

 $H_2S + HgCl_2 = HgS + 2HCl.$ 

It should not be forgotten that mercuric fulminate is an explosive substance, but by keeping it constantly moist there is little chance of its doing any harm. The entire operation must be conducted out of doors on account of the noxious fumes given off.

- A.—Occurs in colourless, tubular crystals.
- S.—Freely soluble in water, insoluble in alcohol.
- D.—The most characteristic test for hydroxylamine is its property of precipitating red cuprous oxide when it is warmed with a solution of ammonio-sulphate of copper. Silver chloride is also at once blackened by it, and solutions of it boiled with caustic soda liberate ammonia gas, recognisable by its odour. Tincture of iodine, or a solution of iodine in potassium iodide, is at once decolorised by it.
- P.—Ammonium chloride is sometimes used as an adulterant, a fraud readily detectable by adding a strong solution of tartaric acid, followed by one of sodium acetate, when, if ammonium chloride is present, a crystalline precipitate will form.
- U.—Employed as a developer for silver bromide in the same way as pyrogallol, etc. As the solution of this substance, although a deoxidising agent, is said not to absorb atmospheric oxygen, it obviously possesses great advantages over the other developers employed in photography.

### Hydriodic Acid.—HI.

This is also a solution of a gas in water, and is prepared like the

hydrobromic acid (q.v.)

(1.) By the action of water upon phosphorus triodide, thus: Into a dry 10oz. flask put 2oz. amorphous (red) phosphorus and 4oz. finely powered iodine, both substances having been previously dried, the phosphorus in the hot water bath, the iodine in a desiccator over sulphuric acid. Gently warm the flask until combination is seen to occur, and having provided the flask with a rubber cork, pierced with two holes, connect to one of these a wide bent glass tube leading into a bottle containing 6oz. of water, beneath the surface of which the end of this tube dips very slightly, and push through the other a thistle funnel drawn off to a fine point. Through this latter let water fall drop by drop, when hydriodic acid will be formed, and will be absorbed by the water in the bottle. When 3oz. of water have been added in this way the contents of the flask should be heated almost to dryness to utilise the last traces of the hydrobromic acid. The acid so obtained contains free iodine, which may be removed by adding caustic soda in quantity just sufficient to decolorise it, and then redistilling the whole.

(2.) A process similar to that used for hydrobromic acid will also answer in this case. If sulphuretted hydrogen is passed through water, the iodine should be finely powdered and suspended in the liquid. If carbon disulphide is employed, the iodine should be

dissolved in twice its weight of that liquid.

The other processes described under hydrobromic acid will not

answer to prepare this compound.

A —A heavy, strongly acid liquid, always darkly coloured from the presence of more or less free iodine.

D.—See Tests for Iodides.

U.—Employed in the preparation of certain iodides.

### Hypochlorites, Tests for.

Solid salts treated with hydrochloric acid liberate chlorine,

readily recognisable by its smell.

Solutions of the hypochlorites give the following reactions:—(1) with silver nitrate, a white precipitate; (2) with manganese chloride, a dark-brown precipitate; (3) they decolorise indigo solution.

### Indiarubber.

Syn., Caoutchouc.

This consists chiefly of a hydrocarbon, represented by the formula C<sub>4</sub>H<sub>7</sub>, but various extraneous matters are always present

as well.

C.—Several tropical plants, chiefly the Hævæa guianiensis and the Siphonia (iatropha) elastica, yield a milky exudation when incisions are made in their bark. Successive layers of this are spread over clay bottle-shaped moulds, which are broken when the layer attains a certain thickness, and the product is known as raw or bottle rubber, in which state it is imported from Brazil

and Central America. It is always of a dark colour, said to be due to the smoke of the open fires over which it is dried. To purify it the raw material is washed in boiling water, cut up into small pieces, again washed by being passed through iron rollers, upon which a jet of boiling water plays, and finally dried in non-actinic light, as ordinary daylight oxidises it more or less.

This purified rubber is masticated by passing it through fluted rollers, or moulded into blocks by forcing it in a soft state into

cast iron moulds, in which it remains until set.

A.—Pure or masticated rubber is a light brown elastic substance, softening readily in hot water, and melting without swelling out at

a gentle heat.

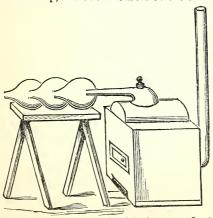
S.—Completely soluble in ether, carbon, disulphide, naphtha, turpentine, benzole, and chloroform. Probably the best solvent for rubber consists of a mixture of one volume of methylated ether with two volumes of benzolene. An ounce of such a mixture will

easily dissolve 20 grains of rubber.

U.—A solution of rubber is occasionally used for mounting prints. The rubber for this purpose should be nearly colourless, but a more or less oxidised (as evidenced by its dark colour) sample can be utilised by digesting it with methylated spirit until it becomes nearly white. The very best rubber for dissolving is, however, got by cutting a block of rubber in two and removing the central portions of it. If benzole is employed, care must be taken that it is as anhydrous as possible. A solution of rubber is also employed as a substratum in certain dry processes.

#### Iodine.-I.

This element occurs in sea water as calcium iodate, from which certain plants, chiefly fuci and laminariæ, extract it, the ash of which constitutes kelp, one of the sources of the element.



C.—To obtain iodine from kelp this is treated with hot water, and the liquid concentrated by evaporation, when sodium sulphate

and carbonate and potassium chloride crystallise out. The liquid is then mixed with sulphuric acid, which decomposes the sodium thiosulphate and sulphide present into sodium sulphate (which on further concentration is deposited in crystals), and precipitates the calcium as calcium sulphate. The liquid is, lastly, mixed with a certain quantity of manganese peroxide (determined by the amount of iodine present), and distilled in the apparatus figured in the text, with the addition of a further quantity of sulphuric acid, when the following decomposition occurs, the calcium iodate having been converted by the icineration of the seaweed into calcium iodide, and this by the action of the sulphuric acid and of the sodium salts present into sodium iodide:  $2\mathrm{NaI} + 3\mathrm{H}_2\mathrm{SO}_4 + \mathrm{MnO}_2 = \mathrm{I}_2 + 2\mathrm{NaHSO}_4 + \mathrm{MnSO}_4 + 2\mathrm{H}_2\mathrm{O}$ . When no more iodine is evolved the receivers are exchanged for others, and more manganese peroxide is added, when bromine is liberated.

Another process consists in passing chlorine through the liquid obtained by lixiviating the kelp, when iodine is set free. The brown liquid is then skaken up with petroleum naphtha, in which the iodine dissolves, and this, on treatment with caustic soda, yields sodium iodide and iodate thus,  $3I_2 + 6\text{NaOH} = 5\text{NaI} + \text{NaIO}_3 + 3H_2\text{O}$ , and this, after having been distilled to dryness to recover the naphtha, is heated with hydrochloric acid, when the following decomposition occurs:  $5\text{NaI} + \text{NaIO}_3 + 6\text{HCl} = 6\text{NaCl} + 3H_2\text{O} + 3I_2$ .

A third and much more economical process consists in subjecting the dry seaweed itself to destructive distillation in closed vessels instead of burning it, when acetic acid, naphtha and tar are got, whilst the residue of porous charcoal contains all the iodine which is recovered from it by lixiviation, followed by the usual treatment.

Iodine is also present in Chili saltpetre (sodium nitrate), and much of the iodine met with in commerce is derived from that source.

L.—To obtain pure iodine the following process answers well:—Mix in a mortar five ounces of commercial iodine with 7½ ounces of water and 3½ ounces of potassium iodide, and triturate the whole until the iodine dissolves. When this occurs filter the solution through asbestos or glass wool into 150 ounces of water, collect the precipitated iodine on glass wool or asbestos, wash it well with distilled water, and dry it on a porous tile. When dry, place the iodine in a glass beaker, gently heat it as long as aqueous vapour mixed with a little iodine escapes, and when this ceases cover the beaker with a larger one, the outside of which is kept cool by means of a wet cloth. On the inside of this second beaker, pure iodine will condense in thin spangles.

A.—Occurs in thin, dark coloured lamine, having a metallic lustre and a peculiar smell. Being somewhat volatile, it is best kept in a glass stoppered bottle.

S.—Sparingly soluble in water, fairly soluble in alcohol, readily soluble in an aqueous or alcoholic solution of potassium iodide.

D.—It colours the skin a transient yellow, and turns starch paste a deep purple. Iodine, in presence of chlorine and bromine, is detected by strongly acidulating the solution and adding hydrogen peroxide to it, when the liquid will be coloured yellow by the liberated iodine. Another plan consists in adding a mixture of copper and ferrous sulphates, when, if iodine is present, a brown precipitate of cuprous iodide will slowly form.

U.—Employed in the manufacture of various iodides, and for several other purposes.

#### lodides, Tests for.

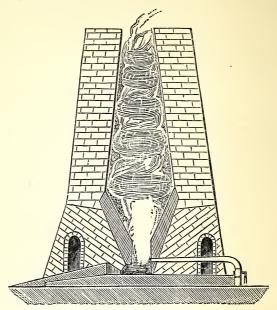
Solid iodides, heated with manganese peroxide and sulphuric acid, liberate violet vapours of iodine. Solutions of the iodides give the following reactions:—(1) With silver nitrate, a yellow precipitate insoluble in the strongest ammonia, which, however, changes its yellow colour to pure white; (2) with copper sulphate, mixed with ferrous sulphate, a brownish precipitate; (3) with mercuric chloride, a yellow or red precipitate, soluble in excess of either mercuric chloride or the soluble iodide; (4) with chlorine or bromine water, or with acetic acid, followed by hydrogen peroxide, a nearly black precipitate, or, in dilute solutions, a reddish-brown coloration.

#### Iron.-Fe.

Occurs abundantly in nature, as—(a.) Magnetic iron ore or ferrous ferrate (Fe<sub>3</sub>O<sub>4</sub>), from which the greater part of the famous Swedish iron is made. (b.) Specular iron ore, or ferric oxide (Fe<sub>2</sub>O<sub>3</sub>), the chief source of Russian iron. (c.) Red hematite, also ferric oxide, occurring in Lancashire. (d.) Brown hematite, or ferric hydroxide (Fe<sub>2</sub>(OH)<sub>6</sub>), occurring abundantly in France. (e.) Clay ironstone and blackband iron ore, two varieties of ferrous carbonate (FeCO<sub>3</sub>) occurring in various parts of England and Scotland, and forming the chief sources of British iron.

C.—Iron is obtained from clay ironstone and kindred ores by first roasting them to drive off carbon dioxide and volatile matters, and then mixing the roasted ore, consisting essentially of ferric oxide, with coal and limestone, and intensely heating the mixture in a blast furnace. This consists of a large structure of brick, cased inside with firebrick, and provided at the bottom with a series of twyers (only one of which is shown in the sketch), through which a powerful blast of hot air is forced. The furnace is fed from the top, and the waste gases are led off by an arrangement not shown in the diagram, and utilised to heat the blast. The reactions which take place are briefly as follows:—The calcium of the limestone unites with the sandy and clayey matters of the ore to form a fusible silicate or slag, whilst the carbon monoxide (CO) resulting from the action of the carbon dioxide (CO2) produced in the hottest portions of the furnace the hot layers of coal (carbon) higher up reacts upon the ferric oxide, converting it into metallic iron in accordance with the equation  $3CO+Fe_2O_3=Fe_2+3CO_2$ , and the

metallic iron so produced unites with a portion of the carbon of the coal to form cast iron, a variety of iron containing about 5% of carbon, silicon, and other matters. The cast iron so formed



gradually sinks, and having been melted by the intense heat nearest the twyers is tapped off from time to time and cast into

bars or pigs.

To produce wrought iron (a purer variety of the metal, distinguished from cast iron by its malleability and comparative infusibility), the cast iron is melted in a species of reverberatory furnace called a puddling furnace, and by being kept constantly stirred whilst a current of air is led over its surface the greater part of the carbon and silicon is burnt out. Wrought iron, as might be expected, is much more expensive than cast iron, and contains on an average 99°/o of pure iron. Ordinary tacks form a convenient source of it. A specially pure variety of wrought iron wire, containing 99.8°/o of metal, can be obtained from most chemical dealers

#### Steel

is either wrought iron, which has been caused to combine with about  $1\frac{1}{2}$ , of carbon by strongly heating wrought iron with charcoal powder (cemented steel), or it is cast iron which has been partially decarburised by blowing air through it whilst in a molten

state (bessemer steel). The first process yields the purer variety of steel employed for edged tools, etc., whilst the latter yields a much cheaper variety of steel employed for tramway rails, ordnance, girders for bridges, etc.

A.—Iron in a perfectly pure condition is a silver-white soft metal, having a texture like vegetable fibre, and a spec. grav. of 7.8. As met with in commerce even the purest varieties of iron are more or less superficially oxidised, due to the carbon dioxide and moisture of the atmosphere coating the metal with rust or ferric oxide.

S.—Soluble in sulphuric acid to form ferrous sulphate—a fact sometimes made use of to prepare that substance—and in most other acids yielding salts of those acids.

U.—Employed as such in ferrotype plates, which are merely thin sheets of best Russian iron coated with black varnish, and also in the form of wire, etc., to prevent solutions of ferrous salts from oxidising in presence of air. Thus, if ferrous sulphate is employed the presence of free metallic iron will tend to reconvert any ferric sulphate which might be formed into ferrous sulphate in accordance with the equation,  $Fe_2(SO_4)_3 + Fe = 3FeSO_4$ .

#### Isinglass.

A pure variety of gelatine (q.v.), obtained from the swimming bladder of various kinds of fish, the bladders being treated with various substances to remove grease, etc., and then carefully washed and dried. The best isinglass, known as leaf, comes from Astrakan, and is said to be made from the bladders of the sturgeon; inferior varieties are imported from Brazil and Hudson's Bay.

U.—Employed by some workers in the collotype process as a substitute for gelatine.

# Kaolin.

Syn., China Clay, White Clay.

This is really a mixture in varying proportions of aluminium silicate and water with traces of iron, magnesium, potassium, and sodium, and is produced naturally as the result of the decomposition of the felspar of granite (which consists of the minerals quartz, felspar, and mica) by the long-continued action of air and water.

The chief English supplies come from Devon and Cornwall, where the crude clay occurs in thick layers, usually situated at a comparatively small depth beneath the surface. The excavated clay is purified by causing water to slowly flow over it, when the coarser particles of sand remain behind, the clay and fine sand being carried away by the stream of water. The mixture is then led first through long channels with rough stone sides, at the bottom of which the sand is deposited; next through channels with wooden sides, in which the coarse clay is deposited; and finally into pits, where the water is permitted to settle, and at the bottom of which the fine clay collects.

- A.—Occurs as a nearly white, soft, fine powder.
- P.—For photographic uses the clay should be quite free from iron. This can be tested for by boiling the sample with strong hydrochloric acid, nearly neutralising the acid liquid so obtained with ammonia, and adding potassium ferrocyanide, when a blue precipitate will occur if iron is present. Chalk and whiting are occasionally used to adulterate china clay. Such a sample will effervesce on treating it with hydrochloric acid.
- U.—Employed for clearing silver nitrate baths from organic matter, a purpose which it doubtless fulfils by mechanically carrying down such matters. It is also used for clearing solutions of shellac, etc., in alcohol (varnishes), but its use for that purpose is not to be recommended, as, by carrying down the waxy and oily matters, it renders the varnish extremely brittle.

#### Lavender, Oil of.

- C.L.—Made by distilling lavender flowers (*Lavendula vera*) with water. Many varieties are known in commerce, that made at Mitcham, in Surrey, being considered the best. French oil of lavender is, however, very much cheaper, and answers every (photographic) purpose. Oil of spike is the trade name of a very inferior variety made from *L. Spica*.
  - A.—A pale yellow liquid, smelling of lavender flowers.
  - S.—Insoluble in water, freely soluble in alcohol.
- U.—Employed in photography as a solvent for bitumen (q.v.) in certain photo-mechanical processes, as a perfuming agent in many encaustic cerates or pastes, as a solvent for pyroxilin in the making of photo-vitrified enamels, and as an addition to shellac varnishes, in which it is said to enable more shellac to be taken up.

#### Lead.-Pb.

Occurs naturally, combined with other elements, in a large number of minerals, of which galena or lead sulphide (PbS) furnishes most of the lead of commerce.

- L.—The process adopted in England to obtain lead from galena is briefly as follows:—The ore having been freed as completely as possible from foreign matter by picking and washing, is permitted to fall through a hopper on the red-hot bed of a reverberatory furnace (see Copper), where the greater portion of it is converted into lead oxide and sulphate in accordance with the equations (a) 2PbS +  $O_6 = 2PbO + 2SO_2$  and (b) PbS +  $O_4 = PbSO_4$ . When it is judged that this reaction is completed some lime is added, and the furnace temperature considerably raised, when the lead oxide and sulphate react upon each other, yielding metallic lead thus—(c) PbSO<sub>4</sub> + PbS = 2Pb + 2SO<sub>2</sub> and (d) 2PbO + PbS = 3Pb + SO<sub>2</sub>, the lime combining with any siliceous matters present to form a fusible slag.
  - A.—A bluish grey, soft metal.
- S.—Soluble in nitric acid, practically insoluble in dilute hydrochloric and sulphuric acids.

U.—Employed in the manufacture of salts of lead, and for lining sinks, &c. As it is unacted upon by hypo, it could be employed to line wooden-grooved tanks to contain fixing baths for negatives.

#### Lead Salts, Tests for.

The soluble salts of lead are characterised by the following reactions:—(1) With hydrochloric acid, a white precipitate soluble in water, and insoluble in ammonia; (2) with sulphuretted hydrogen, a black precipitate soluble in nitric acid; (3) with potassium chromate, a yellow precipitate soluble in caustic soda; (4) with sulphuric acid, a white precipitate soluble in caustic soda; (5) with caustic soda, a white precipitate; (6) with potassium iodide, a yellow precipitate soluble in water.

#### Lead Acetate.— $Pb(H_3C_2O_2)_2 + 3H_2O$ .

Syn., Plumbic Acetate, Acetate of Lead, Sugar or Lead.

C.L.—Made by dissolving finely-powdered litharge to saturation in an excess of hot acetic acid, and evaporating down the solution  $2H_4C_2O_2 + PbO = Pb(H_3C_2O_2)_2 + H_2O$ .

A.—Occurs in white crystalline masses, having a vinegar-like smell and a sweetish taste.

D.—See Tests for Salts of Lead and for Acetates.

S.—Soluble in three times its weight of cold water, yielding a milky solution, cleared by a little acetic acid.

U.—A dilute solution has been proposed as a hypo eliminator, but it is difficult to see what advantages it possesses, as lead thiosulphate is practically insoluble in water, and would be a most undesirable substance on a silver print, owing to the facility with which it blackens under the influence of the traces of sulphuretted hydrogen present in air.

# Lead Chromate.—PbCrO<sub>4</sub>.

Syn., Chromate of Lead.

C.L.—Prepared by mixing solutions of lead acetate and potassium chromate  $Pb(H_3C_2O_2)_2 + K_2CrO_4 = PbCrO_4 + 2KH_3C_2O_2$ .

A.—A yellow insoluble powder.

U.—Lead chromate and lead oxychloride PbCl<sub>2</sub>·7PbO(Paris yellow) are employed to colour certain fabrics for dark rooms, but owing to the ease with which these compounds are altered by exposure to the atmosphere the use of such fabrics is not to be recommended. Materials coloured by salts of lead are readily recognised by the blackening they undergo on being brought in contact with sulphuretted hydrogen, and by their becoming red when boiled with caustic soda.

# Lead Nitrate.— $Pb(NO_3)_2$ .

Syn., Nitrate of Lead, Plumbic Nitrate.

C.L.—Made by saturating dilute nitric acid with finely powdered litharge, filtering and evaporating down, the solution thus,  $PbO + 2HNO_3 = Pb(NO_3)_2 + H_2O$ .

- A.—Occurs in white octahedral opaque crystals, possessing a sweetish taste.
- S.—Soluble in eight times its weight of cold water, nearly insoluble in alcohol.
  - D.—See Tests for Salts of Lead and for Nitrates.
- U.—Employed, mixed with potassium ferricyanide, in the intensification of wet-plate negatives. The negative being immersed in this solution the silver image becomes converted into a mixture of lead ferrocyanide and silver ferrocyanide, thus,  $3Pb_3Fe_2Cn_{12} + 4Ag_2 = 3Pb_2Fe(Cn)_6 + 2Ag_4Fe(Cn)_6$ , and on then treating the bleached negative with ammonium sulphide both these salts become converted into black sulphides, thus,  $Pb_2Fe(Cn)_6 + Ag_4Fe(Cn)_6 + 4(NH_4)_2S = 2PbS + 2Ag_2S + 2(NH_4)_4Fe(Cn)_6$ .

#### Lithium Bromide,-LiBr.

Syn., Bromide of Lithia.

- C.L.—Made by dissolving lithium carbonate in hydrobromic acid,  $\operatorname{Li_2CO_3} + 2\operatorname{HBr} = 2\operatorname{LiBr} + \operatorname{H_2O} + \operatorname{CO_2}$ , or by mixing equivalent proportions of lithium sulphate and calcium iodide in concentrated aqueous solution, evaporating to dryness, and dissolving out the lithium bromide with alcohol. The change is thus represented— $\operatorname{Li_2SO_4} + \operatorname{CaI_2} = 2\operatorname{LiI} + \operatorname{CaSO_4}$ .
  - A.—Occurs in nearly transparent crystalline plates.
  - S.—Freely soluble in water and in alcohol.
  - D.—See Tests for Salts of Lithium and for Bromides.
  - U.—Employed in emulsion making.

# Lithium Chloride.-LiCl.

- C.L.—Prepare like the bromide.
- A.—Occurs in confused deliquescent crystals.
- D.—See Tests for Lithium Salts and for Chlorides.
- S.—Freely soluble in water, nearly insoluble in alcohol.
- U.—Employed in gelatino-chloride emulsions.

#### Lithium Iodide.-LiI.

- C.L.—Prepared like the bromide, but if the second process is adopted the evaporation must take place in *vacuo*, or the salt will be more or less decomposed.
  - A.—Occurs in yellowish crystals.
  - S.—Freely soluble in water and in alcohol.
  - D.—See Tests for Lithium Salts and for Iodides.
  - U.—Employed in iodising collodion.

# Lithium Salts, Tests for.

Solid salts of lithium, moistened with a little hydrochloric acid and held on a platinum loop in the colourless Bunsen flame, colour it an intense crimson. Solutions of lithium salts give the following reactions:—(1.) With sodium phosphate, in alkaline solutions, a white precipitate, provided sufficient lithium is present. (2.) With sodium carbonate a white precipitate in concentrated solutions.

#### Litmus.

A blue colouring matter, reddened by acids.

C.—Made from the Rochella tinctoria, or orchella-weed; the Lecanora tartarea, or rock moss, and several species of Variolaria, by permitting the dried plants to ferment in presence of ammonia and potassium carbonate. When the whole has become violet in colour, stale urine and lime is added, and this causes another fermentation, during which the colour changes to blue. The whole is finally ground up with chalk or gypsum (calcium sulphate) and a little indigo, and made up into tablets, which, when dry, are roughly broken up into small grains. The blue colour is due to azo-litmin, C<sub>7</sub>H<sub>7</sub>NO<sub>4</sub>.

A.—Occurs in largish grains, or in rough lumps.

S.—Treated with water, or alcohol, a portion dissolves, colouring the liquid blue, but a considerable residue remains undissolved.

U.—Employed in solution, or as litmus paper, to indicate whether a solution is neutral, acid, or alkaline. Its indications are not, however, reliable in presence of carbon dioxide, or of organic acids, or their salts.

Litmus solution is made by digesting powdered litmus at a gentle heat with six times its weight of water, filtering the solution, dividing the filtrate into two portions, gradually adding dilute hydrochloric acid to one portion until it is just coloured red, and then mixing this with the other half. Blue litmus paper is made by dipping white blotting-paper in this solution and drying it. Red litmus paper by using litmus solution, reddened by hydrochloric acid.

# Magnesium.—Mg.

C.—Prepared by decomposing anhydrous magnesium chloride by heating it with metallic sodium, in accordance with the equation  $\mathrm{MgCl_2} + \mathrm{Na_2} = 2\mathrm{NaCl} + \mathrm{Mg}$ . Of late years magnesium has fallen considerably in price, owing to improvements in the manufacture of sodium.

A.—A silvery white, somewhat brittle metal, occurring in wire, ribbon and powder.

D.—Dissolved in sulphuric acid, magnesium forms magnesium sulphate, which answers to the usual reactions. (See Tests for Salts of Magnesium.)

U.—Employed in photography as a source of artificial light, as it burns brilliantly in air, or in oxygen, forming magnesium oxide, or magnesia; thus, Mg + O = MgO.

The wire or ribbon may be burnt in a spirit lamp or gas flame, keeping up the supply of wire as fast as it burns, by hand or by means of one of the many automatic-feed lamps introduced for that purpose. The powder is burnt by being blown or projected through the flame either alone or mixed with about twice it weight of finely powdered potassium chlorate. In the latter case a match will set fire to a heap of it, the oxygen being supplied by the potassium chlorate.

# Magnesium Bromide.— $MgBr_2 + 3H_2O$ .

Syn., Bromide of Magnesia.

- C.L.—Prepared by digesting magnesium powder with bromine and water, thus— $Mg + Br_2 = MgBr_2$ ; or better, by dissolving calcined magnesia (magnesium oxide) in hydrobromic acid,  $MgO + 2HBr = H_2O + MgBr_2$ . When solution is complete the liquid must be evaporated down in a desiccator over sulphuric acid, as even at  $100^{\circ}C$  the salt decomposes more or less.
  - A.—Occurs in deliquescent crystals.
  - D.—See Tests for Salts of Magnesium and for Bromides.
  - U.—It has been employed to iodise collodion.

# Magnesium Chloride.—MgCl<sub>2</sub>.

Syn., Chloride of Magnesia.

- C.L.—Prepared by saturating hydrochloric acid with calcined magnesia,  $2HCl + MgO = MgCl_2 + H_2O$ , then adding a quantity of ammonium chloride equal to three times the weight of magnesia taken, evaporating to dryness, and finally igniting gently until fumes cease to be evolved. The ammonium chloride appears to prevent the decomposition of the magnesium chloride, and the addition of ammonium bromide and iodide would doubtless enable magnesium bromide and iodide to be prepared in a similar way.
- A.—Occurs in white semi-crystalline and very deliquescent masses.
  - S.—Freely soluble in water, nearly insoluble in alcohol.
  - D.—See Tests for Magnesium Salts and for Chlorides.
  - U.-Employed in gelatino-chloride emulsions.

# Magnesium Iodide.—MgI<sub>2</sub>.

Syn., Iodide of Magnesia.

- C.L.—Prepared like the bromide (q.v.)
- A.—Occurs in brownish deliquescent crystals.
- S.-Freely soluble in water, fairly soluble in alcohol.

D.—See Tests for Salts of Magnesium and for Iodides.

U.—It has been employed in collodion.

# Magnesium Sulphate. $-MgSo_4 + 7H_2O$ .

Syn., Sulphate of Magnesia, Epsom Salts.

- C.—Made by dissolving finely powdered dolomite (magnesium calcium carbonate) in sulphuric acid, filtering off the insoluble calcium sulphate and evaporating down the filtrate. The change is thus represented  $CaCO_3MgCO_3 + 2H_2SO_4 = CaSO_4 + MgSO_4 + 2H_2O + 2CO_2$ .
- L—A pure product may be obtained by dissolving ordinary Epsom salts in half its weight of boiling water, filtering the hot solution and permitting it to cool, or by dissolving calcined magnesia in sulphuric acid.
  - A.—Occurs in prismatic needle-shaped crystals.
- S.—Soluble in half its weight of boiling and one and a half times its weight of cold water. Insoluble in alcohol.
  - D.—See Tests for Magnesium Salts and for Sulphates.
- U.—Magnesium sulphate has a slight hardening effect upon gelatine, and has for this reason been proposed as a remedy for frilling. A solution of it is used as a test for phosphoric acid or its salts, with which it gives in presence of ammonia a white precipitate of magnesium ammonium phosphate (Mg NH<sub>4</sub> PO<sub>4</sub>).

# Magnesium Salts, Tests for.

Solutions of these salts give the following reactions:—(1) With sodium hydroxide a white precipitate; (2) with ammonium carbonate (in absence of chlorides) a white precipitate; (3) with ammonium hydroxide (in absence of chlorides) a white precipitate; (4) with sodium phosphate (in presence of ammonia) a white precipitate.

#### Mastic.

Syn., Gum Mastic.

A resinous substance obtained from the lentisc or mastic shrub (Pistachia lentiscus), a native of the Mediterranean coasts, of the Canary Islands, and of Hindostan. The chief commercial supplies come from Chios, and are all classified into four varieties:—

(1) Cake mastic, made up of large pieces, and considered the best; (2) large tear mastic; (3) small tear mastic; (4) coarse mastic.

An inferior kind, known as East Indian mastic, is imported from Hindostan.

- A.—A pale yellow or greenish, somewhat soft, resin.
- S.—Freely soluble in alcohol, ether, benzole, and chloroform.
- P.—Distinguished from sandarac (q.v), sometimes fraudulently substituted for it, by the fact that it softens in the mouth.
  - U.—Enters into the composition of many varnishes.

# Methylated Spirit.

Syn., Methylated Alcohol.

A mixture of 90 parts by weight of rectified spirit and 10 parts by weight of purified wood spirit. It is permitted to be sold duty free, a yearly license of £10 10s. being, however, charged to those who prepare it, and a yearly license of 10s. to those who retail it.

Methylated spirit can be rectified in the ordinary way (vide Alcohol), and answers as well as pure alcohol for most purposes.

Methylated spirit can be easily made strong enough for varnish making by shaking it up with dry potassium carbonate in the proportion of 4oz. of carbonate to every gallon of spirit. After a week the upper layer is decanted off. This simple process will bring up the spec. grav. of an ordinary sample to 81. Of course spirit so strengthened will contain traces of potassium carbonate, but this does not in the least interfere with its use for the purpose indicated.

Finish is methylated spirit, containing 3oz. to the gallon of shellac or sandarac, and is permitted to be sold without the annual license, for which reason it is often supplied by small dealers when methylated spirit is asked for. It may be distinguished from the latter by becoming milky when diluted with water, and by giving a smoky flame when burnt in a spirit lamp. It is, of course, quite unfit for any photographic purpose except varnish making. If no other spirit is available, finish can be converted into methylated spirit by distillation.

Methylated spirit can be distinguished from pure alcohol by its smell, and by the fact that it becomes brown when mixed with its own volume of sulphuric acid.

The following methods have been devised for deodorising methylated spirit:—(1). By distilling it over Pears' scentless or any other good resin-free neutral soap cut into fine shreds, using a quarter-pound of soap for every two ounces of spirit. It is best in carrying this out to return the distillate to the retort, and re-distil, and not to push the distillation to dryness. (2.) By mixing 45 grains of finely-powdered potassium permanganate with every gallon of the spirit, followed by 90 minims of strong sulphuric acid. After a week 3 ozs. of barium carbonate are added to the mixture, and the whole redistilled. (3.) By mixing with the spirit 2 % by volume of a mixture of 2 ozs. strong sulphuric acid, and 1 oz. of a cold saturated solution of potassium dichromate, and after a week removing the excess of sulphuric acid with barium carbonate, and redistilling the filtrate. As methyl alcohol has a lower boiling point than ethyl alcohol, this circumstance can be utilised to approximately determine the percentage of methyl alcohol in a sample of methylated spirit. To carry out the test a sample of pure alcohol is reduced by mixing it with water to the same spec. grav. as the sample of methylated spirit to be tested, and the boiling points of each are then determined. Then every 3 3°C. difference between the boiling points corresponds to 10 % of methyl alcohol in the sample.

# Methylic Chloride. - CH<sub>3</sub>Cl.

Syn., Chloride of Methyl.

C.L.—Prepared on a large scale from the Trimethylamine obtained by distilling the refuse of the beet-sugar manufactories. This is neutralised with hydrochloric acid and heated, when it splits up into methylic chloride, trimethylamine, methylamine and hydrochloric acid; thus:— $_3N(CH_3)_3$  HCl = 2 CH $_3Cl$  + 2  $N(CH_3)_3$  +  $NH_2CH_3$  + HCl.

A.—A very volatile liquid boiling at 23°C., and which must on that account be preserved in hermetically sealed vessels, on a large scale in strong steel cylinders, and on a small scale in sealed glass tubes.

U.—Employed in the manufacture of methylanilin (q.v.)

**Methyl Orange.**— $C_6H_4$  (SO<sub>3</sub>Na)  $N_2C_6H_4N$  (CH<sub>3</sub>)<sub>2</sub>. Syn., Sodium Dimethyl-amido-azobenzene-sulphonate, Helianthin,

Poirier's Orange, Tropœolin, Gold Orange, Mandarin Orange.

C.L.—Prepared by the action of methyl anilin upon diazobenzene sulphonic acid.

A.—Occurs as a yellowish brown powder.

S.—Soluble in water to an orange yellow solution; nearly insoluble in alcohol.

U.—Employed as an indicator (vide Volumetric Analysis, part V.) in the estimation of sulphuric, nitric, and hydrochloric acids, being more delicate than litmus and possessing the advantage of being unaffected by carbon dioxide. It cannot be used, however, with organic acids, as its indications are then unreliable. Acids change its colour to red, and alkalies bring back the red solution to its original yellow colour.

# Mercury.—Hg.

Syn., Quicksilver.

Occurs native as such and in combination with sulphur as cinnabar or mercuric sulphide (HgS).

C.—Prepared by distilling the cinnabar itself in presence of air, or in absence of air, mixed with lime. In the first case it decomposes into metallic mercury which is condensed, and into sulphur dioxide gas which escapes thus: HgS+O<sub>2</sub>=Hg+SO<sub>2</sub>; in the second it is decomposed into mercury and calcium sulphide and sulphate in accordance with the equation—4HgS+4CaO=4Hg+3CaS+CaSO<sub>4</sub>, the latter substances remaining behind and the mercury escaping and being condensed in suitable receivers.

L.—To prepare pure mercury the commercial liquid is subjected to distillation, best done in an iron retort, or, if this is out of the question, most of the impurities may be removed by treating the liquid with a large volume of dilute nitric acid. This latter process is not, however, an economical one, as a good deal of the

mercury itself dissolves in the acid. Another method of purification consists in vigorously agitating the mercury with some finely powdered sugar, and then filtering the whole through a paper cone, the apex of which has been punctured.

S.—Mercury dissolves in cold nitric acid, yielding mercurous or mercuric nitrate, or a mixture of both, and in boiling sulphuric acid, yielding mercuric sulphate. Hydrochloric acid is without action upon it.

D.—Mercury dissolved in nitric acid answers to the usual tests (see salts of mercury).

P.—Commercial samples invariably contain tin, lead, zinc, or bismuth. Such samples are known by the metal leaving a track or trail when a globule of the metal is caused to roll over clean glass.

U.—Employed in the manufacture of mercury salts.

#### Mercuric Chloride.—HgCl2.

Syn., Bichloride of Mercury, Corrosive Sublimate.

C.L.—Prepared by heating two parts by weight of metallic mercury with three parts by weight of strong sulphuric acid, and evaporating to complete dryness, when mercuric sulphate remains, Hg+2H<sub>2</sub>SO<sub>4</sub> = HgSO<sub>4</sub> + 2H<sub>2</sub>O + SO<sub>2</sub>. The mercuric sulphate so obtained is then thoroughly mixed in a mortar with 1½ times its weight of common salt and sufficient manganese peroxide to colour the whole brown, and the mixture is then placed (on a small scale) in a florence flask so as to fill about one-eighth of it, and strongly heated. The mercuric sulphate suffers decomposing thus: HgSO<sub>4</sub>+2NaCl=Na<sub>2</sub>SO<sub>4</sub>+HgCl<sub>2</sub>, the sodium sulphate remaining behind and the mercuric chloride escaping in vapour and condensing on the upper portions of the flask. At the conclusion of the experiment the lower portion containing the sodium sulphate removed, when the pure mercuric chloride can be easily detached from the neck and sides unmixed with sodium sulphate.

Mercuric chloride can also be readily prepared by dissolving mercuric oxide (red oxide of mercury) in hydrochloric acid and evaporating down the solution. This change is represented by  $HgO+2HCl=H_2O+HgCl_2$ .

A.—Occurs in fine, white needle-shaped crystals, and in white, heavy lustrous masses having a crystalline fracture.

S.—Soluble in alcohol, ether, and water, its solubility in the latter being increased by the presence of hydrochloric acid, or of ammonium chloride.

D.—See Tests for Chlorides and for Salts of Mercury.

U.—Employed in intensification. When caused to act upon the deposit of silver constituting the photographic image (after fixation) it is deprived of a portion of its chlorine, white silver chloride and mercurous chloride (calomel) being formed thus:  $2Ag+2HgCl_2=2AgCl+Hg_2Cl_2$ . These white compounds may be blackened by any of the following methods:—

1.—By treatment with ammonia—

Dimercuroso-ammonium chloride.

 $Hg_2Cl_2+2NH_3=NH_2Hg_2Cl+NH_4Cl$ 

the blackened image consisting of dimercuroso-ammonium chloride.

2.—By treatment with any soluble sulphide, say that of ammo-

nium, sodium, or potassium-

 $Hg_2Cl_2 + 2AgCl + 2(NH4)_2S = Hg_2S + Ag_2S + 4NH_4Cl$ , the blackened image consisting of a mixture of mercurous and silver sulphides.

3.—By treatment with sodium sulphite—

$$\begin{array}{l} 2 \text{Hg}_2 \text{Cl}_2 + 4 \text{AgCl} + 8 \text{Na}_2 \text{SO}_3 = \text{Ag}_2 + \text{Hg} + 8 \text{NaCl} + \\ 3 \text{Hg} (\text{NaSO}_3)_2 + 2 \text{AgNaSO}_3 \end{array}$$

the blackened image consisting of silver and mercury.

4.—By treatment with any of the usual dry plate developers—say, ferrous oxalate—

 $\frac{\text{Hg}_2\text{Cl}_2 + 2\text{AgCl} + 4\text{FeC}_2\text{O}_4 + 2\text{K}_2\text{C}_2\text{O}_4}{2\text{Fe}_2(\text{C}_2\text{O}_4)_3 + 4\text{KCl}} = \text{Ag}_2 + \text{Hg}_2 + \frac{1}{2}$ 

the blackened image consisting of silver and mercury.

Mercuric chloride is an irritant poison, three grains having been known to cause death, hence too great care cannot be employed in using it. The symptoms of poisoning by mercuric chloride are a metallic taste in the mouth, pains in the throat and stomach, vomiting of blood, diarrhea, feeble pulse, and cold skin.

White of egg is a good antidote, or recently precipitated ferric sulphide, made by adding ammonium sulphide or liver of sulphur to ferric chloride. Failing either of these, flour paste made with milk may be given, followed by an emetic of mustard and water.

#### Mercuric Salts, Tests for.

Soluble mercuric salts give the following reactions:—(1.) With sulphuretted hydrogen, a black precipitate, insoluble in nitric acid. (2.) With sodium hydroxide a yellow precipitate. (3.) With stannous chloride a white precipitate, becoming grey if the stannous chloride is in excess. (4.) With potassium iodide a yellow, scarlet, or vermilion precipitate, readily soluble in excess. (5.) With ammonium hydroxide a white precipitate.

#### Naphtha.

A term used to denote the following substances:-

- 1. Wood naphtha or pyroxilic spirit, obtained by the destructive distillation of wood, and employed in the manufacture of methylated spirit (q.v.). It is really impure methyl alcohol (q.v.).
- 2. Coal naphtha, a liquid obtained by distilling coal tar, and from which benzole (q.v) is got.

3. Mineral or shale naphtha, a substance obtained by the fractional distillation of petroleum or shale oil, that obtained from the former source being generally known as mineral, that from the latter as shale naphtha. The liquid products designated under the generic name of mineral naphtha are subdivisible into

#### Cymogene,

consisting of a mixture of butane  $(C_4H_{10})$  and pentane  $(C_5H_{12})$ . This is a very volatile liquid, having a spec. grav. of about 6, and is used in refrigerating machines.

# Rhigolene,

a liquid consisting chiefly of pentane, and having a spec. grav. of about .63.

#### Gasolene or Canadol,

a liquid used for carburetting water gas, and having a spec. grav. of  $\cdot 64$  to  $\cdot 67$ . It consists chiefly of hexane  $(C_6H_{14})$ .

A mixture of the two last liquids is sold commercially as petroleum ether.

#### Benzine Naphtha,

a liquid having a spec. grav. of 68 to 7, and employed in varnish making.

#### Benzine,

a liquid having a spec. grav. of about .72, and used as a substitute for turpentine.

A mixture of the two last liquids is sold as petroleum spirit or benzoline.

- A.—Of these benzoline is used in photography as a solvent for indiarubber, and is met with in commerce as a volatile, mobile, colourless liquid, having a rather pleasant smell.
- S.—Quite insoluble in water, but miscible in certain proportions with alcohol, and in all proportions with ether, chloroform, benzole, coal tar naptha and turpentine. It will easily dissolve rubber, mastic, dammar, paraffin and wax, and with difficulty shellac; but by mixing it with ammonium carbonate its solvent action upon the latter is greatly increased.
- P.—If of good quality a drop placed on the palm of the hand should evaporate without leaving any after-smell, and when evaporated to dryness at 100°C., no oily residue should remain. If water is present this can be removed by shaking it up with dry plaster of Paris.
- D.—Benzoline is distinguished from benzole, or from coal-tar naphtha by the fact that it dissolves liquified carbolic acid, a substitute quite insoluble in the latter liquids. It may also be distinguished from these by leaving a piece of bitumin in the liquid which will dissolve in benzole or coal-tar naphtha, but will remain unaffected by benzoline.

U.—Employed as a solvent for indiarubber, and to a minor extent for removing grease spots from studio curtains and carpets. It must not be forgotten that benzoline is inflammable and that its vapour forms with air a highly explosive mixture.

Naphthalene.—C<sub>10</sub>H<sub>8</sub>.

- C.—Obtained as the final product of the destructive distillation of coal-tar. The crude substance so obtained is pressed to expel the liquids remaining in its interstices and then dissolved in boiling alcohol, from which, on cooling it crystallises out.
- A.—Occurs in translucent crystals, smelling of coal gas and melting at 80° C.
  - U.—Employed in the preparation of Pnthalic anhydride (q.v.)

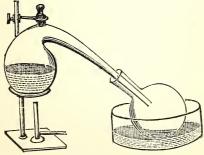
#### Nessler's Solution.

- L.—Made by dissolving 30 grains of potassium iodide in 1½ drachms of distilled water, and boiling this with successive portions of solid mercuric iodide until some of the latter remains undissolved. The liquid is then diluted with 1½ ounces of distilled water, filtered, and the filtrate mixed with 120 grs. of caustic potash dissolved in half an ounce of water, and the whole again filtered.
- U.—Employed as a test for ammonium salts, with which it gives a brownish precipitate or coloration.

# Nitric Acid.—HNO3.

Syn., Aquafortis.

- C.—Made commercially by distilling a mixture of sulphuric acid and sodium nitrate in cast-iron vessels lined with fire-clay, and condensing the acid in stoneware jars placed in cold water. The following equation represents the change  $-2\text{NaNO}_3 + \text{H}_2\text{SO}_4 = \text{Na}_2 + 2\text{HNO}_3$ .
- L.—On a small scale the following method yields a concentrated product. Four ounces of recrystallised nitre are thoroughly dried



by being placed in a hot oven for several hours, and then transferred to a 20 oz. stoppered retort, arranged as shown, connected to v

receiver surrounded by cold water. Two and a half fluid ounces of strong sulphuric acid are next introduced by means of a thistle funnel, taking care not to touch the neck of the retort when removing the funnel, and the retort is then gently heated when nitric acid will distil over and collect in the receiver; a change represented by  $\rm KNO_3 + H_2SO_4 = \rm KHSO_4 + HNO_3$ . When one and a-half ounces of acid have collected in the flask the operation should be stopped and the contents of the retort poured out into a dish whilst still hot, as if permitted to cool and solidify it will be found difficult to remove the acid potassium sulphate without fracturing the retort.

To purify a sample of commercial nitric acid containing chlorine and therefore unfit for making pyroxilin, it may be re-distilled over a small quantity of silver nitrate, and samples of commercial acid too weak to use for the same purpose may be dehydrated by redistilling them with their own volume of strong sulphuric acid.

A sample of acid containing an excess of nitrogen peroxide (known by its yellow colour) may be decolorised by blowing dry air through it for some time.

A.—A highly corrosive acid liquid fuming in contact with air if concentrated, colourless if pure, but usually coloured yellow by traces of nitrogen peroxide.

As usually met with the acid contains more or less water, the quantity of true acid varying from 46.6% in aquafortis (spec. grav. 1.29) to 67.6% in double aquafortis (spec. grav. 1.42). The spec. grav. of nitric acid is, provided other matters are absent, a valuable criterion of its strength. The following table gives the spec. grav. at 15°C. of various samples of acid and the percentages of real acid (HNO<sub>3</sub>) which they contain:—

Spec. grav. at 15°C.	Percentage of real acid.
1.530	100.0
1.495	90.0
1.460	80.0
1.423	70.0
1.374	60.0
1.317	50.0
1.251	40 0
1.185	30.0
1.120	20.0
1.089	15.0
1.060	10.0
1.029	5.0

S.—Miscible in all proportions with water. Dissolves most metals with decomposition, converting them into nitrates.

D.—This acid possesses the characteristic property of staining the skin and finger nails yellow. It stains woollen fabrics red, and such stains, unlike those produced by sulphuric and hydrochloric acids are intensified by ammonia. Concentrated nitric acid warmed with iron, copper, mercury, or silver gives off red fumes of nitrogen peroxide, and brucine is changed by it to a characteristic red.

P.—The impurities commonly present in commercial nitric acid are sulphuric acid, detected by diluting the acid and adding barium nitrate, hydrochloric acid detected with silver nitrate and nitrogen peroxide rendered evident by a yellow colour. Water is also generally present in varying quantity (vide supra).

U.—Employed to manufacture silver nitrate and pyroxilin (q.v.) For the latter purpose the acid should be of at least 1.4 spec. gravity.

#### Nitrates, Tests for.

Solid nitrates, heated with copper and strong sulphuric acid, liberate red fumes. Liquids containing nitrates give the following reactions: (1.) Treated with an equal volume of strong sulphuric acid, and allowed to cool, and then mixed with a freshly-prepared and clear solution of ferrous sulphate, carefully added so as to float on the top, a brown ring will be observed at the junction of the two liquids. (2) Mix with a little strong sulphuric acid, and then added to solid brucine, a red solution is produced.

#### Nitrites, Tests for.

Solid nitrites warmed with dilute hydrochloric acid yield brownish red fumes. Liquids containing nitrites give the following reactions: (1.) With silver nitrate a white precipitate, forming only in moderately-concentrated solutions, and soluble in water. (2.) With ferrous sulphate, a brown or black coloration. (3.) With potassium iodide, followed by dilute hydrochloric acid, a claret-red coloration.

#### Nitro-Benzene-C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>.

C.L.—Made by dropping benzol into a cold mixture of equal volumes of sulphuric and nitric acids, and then pouring the red liquid so obtained into a large volume of water, at the bottom of which the nitro-benzene will be found.  $C_6H_6 + HNO_3 = C_6H_5$   $NO_2 + H_2O$ .

A.—A heavy, oily liquid, possessing a strong almond-like odour.

U.—Employed in the preparation of anilin (q.v.)

# Oxalic Acid. $-\mathrm{H_2C_2O_4} + 2\mathrm{H_2O.}$

C.—Prepared on a large scale as follows:—

(1.) From certain plants which contain it in the form of potassium binoxalate (salt of sorrel) KH C<sub>2</sub>O<sub>4</sub>. Such plants are wood sorrel, containing about ·25% of, and common sorrel ·77% of the salt, the latter of which is extensively cultivated in Germany for manufacturing the acid. To prepare oxalic acid from the plant, the leaves are reduced to pulp, treated with water, and the whole allowed to stand for a week, the process being repeated until

all soluble matters are extracted. The liquid is next mixed with kaolin, and allowed to stand, when the vegetable albumin is mechanically carried down with the kaolin. The clear liquid is then concentrated by evaporation, when crystals of potassium binoxalate separate out, and these are converted into oxalic acid by treatment with dilute sulphuric acid thus,  $KHC_2O_4 + H_2SO_4 = KHSO_4 + H_2C_2O_4$ , the less soluble potassium sulphate being

removed by crystallisation.

(2.) By the action of nitric acid on treacle or coarse sugar when a change occurs represented by the following equation: C12H22O11  $+ 18HNO_3 = 6H_2C_2O_4 + 14H_2O + 9N_2O_3$ . To carry out the process a strong aqueous solution of the treacle or sugar is mixed with one per cent. of its volume of sulphuric acid, and permitted to stand, when any lime present will separate out as a precipitate of calcium sulphate. The clear liquid is next mixed with a weight of strong nitric acid equal to that of the treacle, etc., taken and heated to 30°C. for twenty-four hours, after which the whole is permitted to stand for a day or two to permit any impurities to subside. The liquid is then again decanted off, mixed with a weight of sulphuric acid equal to six times that of the treacle, etc., taken, followed by a weight of nitric acid equal to twice that of the sulphuric acid, the nitric acid being added at four intervals twelve hours apart. During the first stage the liquid is kept at 38°C., during the second at 43°C., during the third at 49°C., and during the fourth at 52°C. The whole is finally concentrated by

evaporation, when crystals of the acid separate out.

(3.) By the action of caustic potash, or a mixture of this and caustic soda upon sawdust, the change being represented thus:  $C_6 H_{10} O_5 + 6 KOH + H_2O = 3 K_2 C_2 O_4 + 9 H_2$ , hydrogen being liberated and acid potassium oxalate formed, from which oxalic acid is subsequently got. To prepare the acid by this process a lye of spec. grav. 1.35 is made by dissolving one equivalent (56 parts by weight) of caustic potash and two equivalents (80 parts by weight) of caustic soda in water, and this is then mixed with sawdust in the proportion of 40lbs. of sawdust for every 100 gallons of the lye. To effect this the sawdust is spread evenly over thick iron plates and the lye gradually poured over it. The paste so obtained is then heated for six hours at a temperature of about 200°C, being kept meanwhile constantly stirred. The sawdust gradually disappears, and at the conclusion of the process the mass practically consists of potassium oxalate. The whole is then treated with a little cold water, which dissolves out any excess of alkali, leaving the greater part of the oxalate behind. Boiling water is then added to dissolve the oxalate, and the solution mixed with milk of lime, when caustic potash is formed and insoluble calcium oxalate precipitated, thus  $K_2C_2O_4 + Ca(OH)_2 = CaC_2O_4 + 2KOH$ . The caustic lye is decanted off, mixed with more milk of lime to convert any carbonated into caustic alkali, and used over again; and the precipitated calcium oxalate is treated with sulphuric acid when calcium sulphate is precipitated, and oxalic acid passes into solution thus  $Ca\tilde{C}_2O_4 + \tilde{H}_2S\tilde{O}_4 = CaSO_4$ + H.C.O.

L.—On a small scale pure oxalic may be obtained by the second of these processes, thus: An ounce and three-quarters of powdered sugar candy are gently heated in a flask with nine ounces of strong nitric acid, the source of heat being removed once effervescence commences. On cooling, crystals of pure oxalic acid will separate out, and a fresh supply can be obtained by concentrating the residual liquid. These should be drained free from acid in a funnel plugged with glass wool, re-dissolved in a small quantity of water, and the solution re-crystallised. To purify commercial oxalic acid, dissolve it in boiling water containing 10 per cent. by weight of hydrochloric acid, and cool quickly to get small crystals, which wash thrice with ice-cold water, and finally re-crystallise by dissolving them in a small quantity of boiling water and permitting the solution to cool.

- A.—Occurs in transparent, needle-shaped crystals.
- S.—Readily soluble in water, insoluble in alcohol.
- D.—Heated with strong sulphuric acid, it decomposes into carbon dioxide and monoxide, the latter of which will burn with a blue flame on a light being applied to the mouth of the tube in which the decomposition is effected.
- P.—Usually almost pure, containing at most a trace of sulphuric acid, detected by adding barium nitrate, followed by hydrochloric acid in excess, when some of the precipitate will remain undissolved if sulphuric acid is present.
- U.—Employed to prepare ferric oxalate (q.v.), and for several other minor uses.

Oxalic acid and its salts are poisonous, half-an-ounce of the acid having proved fatal. In the case of the acid itself the symptoms are burning pain in the stomach, with cramps and drawing-up of the legs, accompanied by the vomiting of bloody matters, the throat feeling as if tightly bound with a cord. Bloody purging next occurs, the tongue becomes sore, the mouth swollen and usually white, and in extreme cases this is followed by twitching of the face, delirium and convulsions. The pulse is throughout very weak and slow, and the respiration spasmodic. With the oxalates the symptoms of burning pain in the stomach, vomiting of bloody matter, and bloody stools do not usually occur. The best antidote in cases of poisoning is whiting, chalk, or magnesia suspended in milk.

Oxalates, Tests for.

Solid oxalates, heated with strong sulphuric acid, behave like oxalic acid (q.v.). Solutions containing these salts give the following reactions:—(1) With barium nitrate a white precipitate, soluble in hydrochloric acid. (2.) With calcium chloride a white precipitate, soluble in hydrochloric acid. (3.) With silver nitrate a white precipitate, soluble in nitric acid.

Phthalic Anhydride.  $-C_6H_4(CO)_2O$ .

C. L.—Prepared by carefully mixing on paper an ounce of napthalene (q.v.) with two ounces of finely powdered potassium

chlorate, and then adding the mixture in small quantities at a time to  $8\frac{1}{2}$  fluid ounces of strong hydrochloric acid, when napthalene tetrachloride ( $C_{10}H_8Cl_4$ ) will be precipitated. This is collected on a filter, washed with water until free from acid, and dried spontaneously. It is then placed in a 20oz. flask, and 7oz. of nitric acid (spec. grav. 1·45) added to it in quantities of a drachm at a time. When all the acid has been added, the mixture is evaporated to dryness, and redistilled in a small hard glass retort, when phthalic anhydride passes over.

U.—Employed in the manufacture of eosin (q.v.) and of phenol

phthalein (q.v.).

# Phenol Phthalein. — $C_{20}H_{14}O_4$ . Syn., Dihydroxy-diphenyl phthalide.

C.L.—Made by digesting 10 parts phenol and 5 parts phthalic anhydride with 4 parts of fuming sulphuric acid for several hours, at a temperature of about 130°C, and boiling the residue with water until everything soluble has been extracted. The mass remaining as a residue is dissolved in boiling benzol and permitted to cool, when phenol phthalein will separate out as a yellow powder.

S.—Insoluble in water. Soluble in alcohol.

U.—Employed in alcohol solution as an indicator for organic acids. These do not alter its colour, but alkalies change it to a purple red. Its indications cannot, however, be relied on in presence of either ammonia or carbon dioxide.

## Phosphates, Tests for

Soluble phosphates give the following reaction:—(1.) With barium nitrate, a white precipitate soluble in hydrochloric acid. (2.) With calcium chloride, a white precipitate soluble in hydrochloric acid. (3.) With ferric chloride, a yellowish white precipitate (4.) With magnesium sulphate, preceded by ammonium, hydroxide and chloride, a white precipitate. (5.) With silver nitrate, a yellow precipitate soluble in nitric acid. (6.) With ammonium molybdate in presence of an excess of nitric acid, a yellow precipitate, the production of which is accelerated by gently heating the solution.

#### Platinum. - Pt.

## Syn., Platina.

C.—Ores of this metal are found in the Ural Mountains, in the Andes in Brazil, in Hayti, and in Australia. The ores consist of mixtures in varying proportions of platinum and certain other rare metals. To separate the platinum the ore is fused with lead, and the alloy so obtained treated with nitric acid, which dissolves out almost everything but the platinum. The residue is then acted upon by dilute aqua regia, which dissolves out only the platinum and the remaining lead, and the solution so obtained is then mixed with sulphuric acid and permitted to stand. This precipitates the lead as lead sulphate, and, after filtration, ammonium chloride is added to the liquid when ammonium chloroplatinate (NH<sub>4</sub>)<sub>2</sub>PtCl<sub>6</sub>) falls as a yellow precipitate.

To obtain platinum from this it is first strongly heated, when it decomposes into ammonium chloride, chlorine and platinum thus— $(NH_4)_2PtCl_6=2NH_4Cl+Cl_4+Pt$ , and the spongy platinum so obtained is fused in a lime crucible in a furnace fed with coal gas and oxygen.

- A.—A white, heavy, rather soft metal, somewhat resembling silver in appearance, very infusible, and unacted upon by the atmosphere or by most acids.
  - S.—Soluble in aqua regia, chloroplatinic acid being formed.
- D.—The solution in aqua regia gives the usual reactions (see salts of platinum).
- U.—Employed in the manufacture of potassium chloroplatinite (q.v.)

#### Platinum Salts, Tests for.

Soluble platinum salts give the following reactions:—(1.) With sulphuretted hydrogen a slowly-forming brownish black precipitate. (2.) With ammonium hydroxide a yellow crystalline precipitate. (3.) With ferrous sulphate, on long continued boiling, a black precipitate. (4.) With potassio-ferrous oxalate an immediate black precipitate.

# Potassium Aluminium Sulphate.

 $Al_{\overline{2}}K_{2}(SO_{4})_{4}^{s}\cdot 12H_{2}O.$  $Sun_{*}$ , Potash Alum.

Occurs native near Naples, in Tuscany, Sicily, and in the South of France.

C.—Manufactured from—(1.) Coal shale, a slaty mineral found underlying the coal in South Lancashire and elsewhere. (2.) Alum shale, a bituminous clay found near Whitby, in Yorkshire, at Campsee, near Glasgow, and in various parts of the Continent. (3.) Alum rock, found in most volcanic districts. (4.) Pipeclay, or other clay containing little or no iron. (5.) Rhodonda phosphate, an impure aluminic phosphate coming from the island of that name in the West Indies. (6.) Cryolite, or ice stone (in allusion to its ready fusibility), a double fluoride of aluminium and sodium met with in Greenland. (7.) Bauxite, a mineral obtained from the vicinity of Belfast. To make alum from shale, this is broken up, calcined at a low temperature, and allowed to remain exposed to the air for a considerable period. The calcination deprives the pyrites (FeS2) present of half of its sulphur, which, in contact with the porous shale, combines with atmospheric oxygen and becomes sulphuric anhydride (SO<sub>3</sub>), which immediately reacts upon the alumina present to form aluminic sulphate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>). By exposure to air the residue of ferrous sulphide (FeS) becomes oxidised to ferrous sulphate (FeSO<sub>4</sub>). When the latter change is judged to be complete, the mass is treated with warm water, which dissolves out the ferrous and aluminic sulphates, and on concentration the greater part of the former separates out as green crystals. The liquid is then mixed with carnallite (KCl·MgCl<sub>2</sub>) and boiled, by which means the residual ferrous sulphate is converted into ferrous chloride, potassium and magnesium sulphate being simultaneously formed. The potassium sulphate at once combines with the aluminic sulphate to form alum, which on concentrating the liquid a little separates out as alum meal, the ferrous chloride and magnesium sulphate, being much more soluble, remaining behind in the solution.

To obtain alum from alum rock, this is merely calcined, dissolved in water, mixed with the requisite quantity of potassium sulphate, and the alum crystallised out.

To obtain alum from clay, it is first calcined to peroxidise any iron present and to render the clay porous. The residue is then ground to powder, heated with sulphuric acid until it becomes a stiff paste, and exposed to the air for several weeks, when the aluminic oxide gradually becomes converted into aluminic sulphate, which is converted into alum in the usual way. In dealing with rhodonda phosphate, it is first mixed with coal dust and calcined, then treated with sulphuric acid, which decomposes it into aluminic sulphate and phosphoric acid. The liquid is then mixed with potassium sulphate and the alum crystallised out, and the residue, which contains the phosphoric acid, made into a paste with sawdust, and disposed of for manure.

To make alum from cryolite this is finely ground and boiled with slaked lime when sodium aluminate passes into solution, calcium fluoride being precipitated. The latter is permitted to settle; the liquid syphoned off and mixed with some more finely powdered cryolite, when alumina is thrown down and sodium fluoride passes into solution. The alumina is then carefully washed and converted into alum in the usual way. When dealing with bauxite this is dissolved in sulphuric acid and the iron thrown down as Prussian blue with potassium ferrocyanide, the aluminium sulphate so obtained being dealt with as before.

A.—Occurs in transparent irregular crystals or as a fine white powder.

S.—It dissolves in ten times its weight of cold water, but is insoluble in alcohol.

D.—See potassium and sulphuric acid. Because of the aluminium contained in it it gives with ammonia a white precipitate of aluminic hydroxide.

P.—It should give no precipitate with either potassium ferro or ferricyanide showing absence of iron.

U.—Employed in photography to harden gelatine in the autotype and kindred processes. It has been recommended as an addition to the bath for sensitising albuminised paper, as it appears to prevent the formation of scum, and by at once coagulating the albumen it keeps the print on the surface of the paper. It is obvious that when it is so employed a much weaker silver solution than usual may be made use of without any fear of the albumen dissolving.

#### Potassium Antimoniate. -2KSbO35H2O.

- C. L.—Made by gradually adding one part of finely-powdered antimony to four parts of malted nitre, when the following change occurs:— $28b + 5KNO_3 = 2KSbO_3 + 3KNO_2 + N_2O_3$ . The residue is powdered and washed with warm water to remove the potassium nitrite and excess of nitre, then boiled for a couple of hours with water, when it becomes hydrated and dissolves, and the solution on evaporation yields hydrated potassium antimoniate.
  - A.—Occurs as a dirty white somewhat granular powder.
  - S.—Soluble in warm water, but decomposed by continued boiling.
- U.—Employed as a test for sodium, with which it gives a sparingly soluble heavy crystalline precipitate of sodium antimoniate. Since acids decompose potassium antimoniate, it is essential that the solution to be tested be neutral or alkaline.

#### Potassium Bromide.-KBr.

Syn., Bromide of Potassium, Bromide of Potash.

C. L.—Prepared like the corresponding iodide (q.v.), substituting bromine for iodine, and using a weight of bromine equal to  $\frac{80}{127}$ ths of the weight of iodine directed to be taken.

If pure bromine is employed a pure product will be obtained, but if the bromine contains any chlorine or iodine these will be present as potassium chloride and iodide in the final product.

Commercial samples of potassium bromide can be freed from iodide by dissolving the salt in the smallest possible quantity of water, and adding bromine water in small quantities, at times boiling the solution for some time after each addition. The addition of bromine water is continued until starch paper dipped in the liquid ceases to give the iodine reaction (see Pante), an excess of bromine being avoided. Finally the whole is evaporated to dryness and gently ignited, when the iodine and slight excess of bromine will escape.

- A.—Occurs in white, cubical crystals.
- S.—Soluble in 1½ times its weight of water, insoluble in alcohol.
- D.—See Tests for Potassium Salts and for Bromides.
- P.—Commercial potassium bromide usually contains potassium iodide. To detect this in a rough manner add a little bromine water to a solution of the bromide, and dip starch paper in the liquid, when the paper will be coloured blue if iodine is present. The following are more delicate tests for potassium iodide in presence of bromide:—
- (1.) Dissolve 5 grains of the sample in half an ounce of distilled water, and place the solution beside another tube containing the same quantity of distilled water only. Now with a glass rod moistened with a drop of a 5% solution of palladium chloride stir up the distilled water, and do the same to the bromide solution with the rod again moistened with the palladium chloride, when the slightest trace of iodide will be indicated by a brownish-red coloration.

- (2.) In 3 ounces of distilled water, acidified with a drop of sulphuric acid, dissolve in the cold 150 grains of ferrous sulphate, and 60 grains of copper sulphate, and filter carefully. On adding an excess of this solution to a strong solution of the bromide, a brownish precipitate will slowly form if iodine is present.
- (3.) To a strong solution of the bromide to be tested, add sufficient acetic acid to render it strongly acid, and then an excess of hydrogen peroxide, when a brownish-red coloration will indicate the presence of an iodide.

Potassium bromate is occasionally present in commercial potassium bromide, and is detected by the blue colour which a solution of it, acidified with acetic acid, gives with a mixture of starch paste and potassium iodide.

Potassium chloride is detected by completely precipitating a solution of the bromide with silver nitrate, well washing the precipitate, shaking it up with a cold mixture of two drachms of strong ammonia in 3 ozs. of water, filtering off the liquid, and adding an excess of nitric acid to the filtrate, when a precipitate or milkiness will indicate chlorine.

U.—Potassium bromide is employed in emulsion making in cases where alcohol is not employed, such as in emulsions of silver bromide in gelatine. With silver nitrate it reacts thus, AgNO<sub>3</sub> + KBr = KNO<sub>3</sub> + AgBr, forming potassium nitrate and silver bromide, the latter remaining in suspension in the gelatine. It is also employed as a restrainer in so-called alkaline development, which function it fulfils probably by forming a definite compound with the unaltered silver bromide (represented perhaps by AgBrKBr), more difficult to be decomposed by the developer than is silver bromide itself.

# Potassium Dichromate.—K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.

Syn., Potassium Bichromate, Potassium Anhydrochromate, Bichromate of Potash, Red Chromate of Potash.

C.—The source of this salt is chrome iron ore (FeO·Cr<sub>2</sub>O<sub>3</sub>), found in Russia and America. To make the salt the ore is first strongly heated, then thrown into water, and finely ground, and the powder mixed with potash-lime, obtained by mixing potassium carbonate with slacked lime, and evaporating down the clear liquid with an excess of lime.

This mixture is heated in a reverberatory furnace for several hours, when it becomes converted into a mixture of potassium and calcium chromate and ferric oxide in accordance with the equation  $2(\text{FeO Cr}_2O_3) + 2\text{KOH} + 3\text{CaO} + 6O = \text{K}_2\text{CrO}_4 + 3\text{CaCrO}_4 + \text{Fe}_2O_3$ . The mass is next treated with hot water, when the potassium chromate and calcium chromate dissolve, the ferric oxide remaining behind, and the clear solution is next mixed with potassium sulphate, by which the calcium chromate is converted into calcium sulphate, which is precipitated, and potassium chromate, thus,  $\text{CaCrO}_4 + \text{K}_2\text{SO}_4 = \text{K}_2\text{CrO}_4 + \text{CaSO}_4$ . The clear, yellow liquid is finally concentrated somewhat, mixed with a slight excess of nitric

acid and permitted to stand, when red crystals of the dichromate separate out— $2K_2CrO_4 + 2HNO_3 = K_2Cr_2O_7 + 2KNO_3 + H_2O$ , the more soluble potassium nitrate remaining behind.

- L.—A perfectly pure salt may be prepared from commercial samples by recrystallising them twice.
- A.—Occurs in large, red transparent crystals, which should be well formed and of a uniform colour throughout, without yellowish edges.
- S.—Soluble in ten times its weight of cold, and in three times its weight of boiling water. Insoluble in alcohol.
  - D.—See Tests for Potassium and for Chromates.
- P.—Potassium sulphate and chloride are sometimes present. To test for these make a 2% solution of the salt in water, add to it eight times its volume of a 2% solution of tartaric acid, and let the whole stand 24 hours. At the expiration of this time decant off the supernatant liquid, and test it for sulphates with barium nitrate, and for chlorides with silver nitrate.
- U.—Employed in the autotype process, and in photo-mechanical work, owing to the property it possesses of rendering gelatine and albumen insoluble on exposure to light. According to Eder, the insoluble gelatine is an unstable compound of unaltered gelatine and chromous chromate, potassium chromate being simultaneously formed, a change represented perhaps by  $2K_2Cr_2O_7 = CrCrO_4 + 2K_2CrO_4 + O_2$ , the liberated oxygen attacking and oxidising a portion of the gelatine into formic acid and other compounds.

Potassium dichromate taken internally acts as an irritant poison. The proper antidotes in such a case are magnesia, or even chalk, followed by emetics.

Potassium dichromate is also absorbed by the skin, such absorption being greatly facilitated if abrasions or cuts are present. In manufactories of the salt it attacks the septa of the workmen's noses, in many cases entirely destroying them, but curiously enough never attacking the walls. The liberal use of snuff is said to ensure complete immunity from its effects. It also attacks the skin of the hands more or less, the effects beginning with a violent irritation, and an irresistible desire to scratch the affected parts, which in a short time become more or less ulcerated. The disease sometimes takes the form of a red rash, which ultimately resolves itself into a species of pityriasis, the skin becoming destroyed, and breaking up into scales. If the skin is abraded, the disease is chiefly confined to ulceration, the ulcers gradually increasing in size and depth, and frequently reaching to the bone.

It is said that the use of the citrine ointment of the pharmacopæia has proved an effectual remedy, the mercuric nitrate present in the ointment doubtless converting the soluble and poisonous potassium dichromate into insoluble and harmless mercuric chromate.

In photo-mechanical work, autotype tissue sensitising, etc., the disease takes the form of violent itching and burning at the backs of the fingers, which become covered with pustules which, if scratched, exude a watery fluid. These gradually increase in size, spreading to the back of the hand and then to the under portions of the wrist, the inner surface of the arms being also sometimes attacked. The pustules finally die away, when the covering skin cracks and scales off, leaving painful sores, upon which the bichromate does not appear to act to produce ulceration as it does upon accidentally abraded skin. Curiously enough, this form of the bichromate disease only appears in certain individuals, and in any case only results from long-continued and constant contact of the hands with the bichromate solutions. Rubbing the hands with a mixture of ammonia, carbolic acid, and glycerine is said to prove an effectual cure.

#### Potassium Chlorate.—KClO3.

Syn., Chlorate of Potash.

C.—Prepared by passing chlorine gas through potassium carbonate, slaked lime, and a little water, when the following change occurs—

 $K_2CO_3 + 6Ca(OH)_2 + 6Cl_2 = 2KClO_3 + 5CaCl_2 + CaCO_3 + 6H_2O.$ 

On treating the mixture with boiling water potassium chlorate and calcium chloride dissolve out, and the liquid furnishes, on being evaporated down, crystals of the less soluble potassium chlorate.

Another process consists in passing chlorine through a mixture of slaked lime and water, when calcium chlorhydrate (vide Bleaching Lime) is formed, and on boiling down the solution this is decomposed into calcium chlorate, calcium hydrate, and calcium chloride, thus, 6CaOClOH = Ca(ClO<sub>3</sub>)<sub>2</sub> + 3Ca(OH)<sub>2</sub> + 2CaCl<sub>2</sub>. By mixing the filtered hot solution with potassium chloride, calcium chloride and potassium chlorate are formed, and the latter, being sparingly soluble, separates out.

L —On a small scale the salt may be made by dissolving 300 grains of dry potassium carbonate in two fluid ounces of water, and passing through this the chlorine obtained by warming  $1_{20}^{1}$ . of manganese peroxide with five fluid ounces of strong hydrochloric acid. The initial action is represented by  $K_{2}CO_{3} + Cl_{2} = KCl + KClO + CO_{2}$ . When carbon dioxide gas ceases to escape the liquid is filtered and evaporated down to small bulk, when the potassium hypochlorite decomposes thus,  $3KClO = KClO_{3} + 2KCl$ , and crystals of the comparatively insoluble potassium chlorate separate out. These are collected on a filter, washed with a little cold water, then redissolved in boiling water, and recrystallised.

A.—Occurs in well-defined tabular crystals.

S.—Soluble in sixteen parts of cold and in two parts of boiling water.

- D.—A fragment of potassium chlorate warmed with strong sulphuric acid decomposes with a series of small explosions.
- P.—Potassium chlorate should give no precipitate with silver nitrate, denoting absence of potassium chloride.
- U.—Employed in the platinotype process to increase contrast, which it does by converting some of the potassium chloroplatinite into chloroplatinate, the latter being then unacted upon by the ferrous oxalate produced by the action of light.

# Potassium Chloroplatinite.—K<sub>2</sub>PtCl<sub>4</sub>.

Syn., Platinotype Company's "Red Salt."

- C L.—Made by converting a weighed quantity of metallic platinum into chloro-platinous acid (q.v.), evaporating this to dryness at  $100^{\circ}\mathrm{C}$ , dissolving it in the smallest possible quantity of water, and mixing the solution with a quantity of pure potassium chloride equal to the weight of platinum taken, and also dissolved in the smallest possible quantity of hot water, when the following change occurs:— $H_2\mathrm{PtCl}_4 + 2\mathrm{KCl} = \mathrm{K}_2\mathrm{PtCl}_4 + 2\mathrm{HCl}$ . On permitting the mixture to stand for twelve hours crystals of potassium chloroplatinite will separate out. These are collected on a filter, washed with strong alcohol until the washings are no longer acid, and finally dried in the dark on blotting paper. The "mother liquor," or filtrate from the crystals, contains some unaltered platinum, which may be recovered in the usual way.
  - A.—Occurs in reddish deliquescent crystals.
  - S.—Freely soluble in water, nearly insoluble in alcohol.
- D.—The solution is at once reduced by ferrous oxalate, alkaline hypo, and the usual dry plate developers. On boiling it with a little nitric acid, and then permitting the liquid to cool, it deposits, if sufficiently concentrated, yellow crystals of potassium chloroplatinate.
- P.—The salt should dissolve in water without leaving any residue, and yield a neutral solution.
- U.—Ferrous oxalate reduces it to metallic platinum, thus  $6 \text{FeC}_2 \text{O}_4 + 3 \text{K}_2 \text{PtCl}_4 = 2 \text{Fe}_2 (\text{C}_2 \text{O}_4)_3 + \text{Fe}_2 \text{Cl}_6 + 6 \text{KCl} + 3 \text{Pt}$ , and its use in the platinotype process depends upon this fact.

# Potassium Citrate.—K<sub>3</sub>H<sub>5</sub>C<sub>6</sub>O<sub>7</sub>

Syn, Citrate of Potash.

- C.L.—Prepared by adding potassium carbonate to a solution of citric acid until the solution is neutral and evaporating to dryness  $2H_3H_5C_6O_7+3K_2CO_3=2K_3H_5C_6O_7+3CO_2+3H_2O$ .
  - A.—A white deliquescent semi-crystalline salt.
  - S.—Soluble in water, insoluble in alcohol.
  - D.—See Tests for Potassium and for Citrates.
- U.—Used as a restrainer in alkaline development, and as a preservative of ready sensitised paper.

#### Potassium Cyanide.-KCn.

Syn., Cyanide of Potash, Cyanide.

C.—Made by mixing eight parts of potassium ferrocyanide with three parts of potassium carbonate, both well dried and in fine powder, and fusing the mixture in an iron crucible at a low red heat until a sample taken out on the tip of an iron rod solidifies to a white solid. The change is represented by  $\rm K_4Fe~(Cn)_6+\rm K_2CO_3=5\rm KCn+\rm KCnO+\rm CO_2+\rm Fe.$  When it is complete, the vessel is removed from the fire and left at rest until the iron subsides, after which the clear liquid is poured out on an iron plate and permitted to solidify. So prepared, the cyanide is mixed with cyanate and carbonate, which, however, do not seem to interfere with any of its photographic uses.

L.—Pure potassium cyanide may be made by dissolving caustic potash in absolute alcohol, and passing hydrocyanic acid gas into the liquid, when pure potassium cyanide is deposited in crystals. The hydrocyanic acid gas is conveniently prepared by warming potassium ferrocyanide with dilute sulphuric acid. As the vapour of this substance is intensely poisonous the entire operation is best conducted out of doors. The action of the hydrocyanic acid upon caustic potash is represented thus, KOH + HCn = H<sub>2</sub>O + KCn

A—The commercial variety occurs as white opaque lumps, the pure salt in octahedral crystals, both smelling of bitter almonds. The salt should be kept in a stoppered bottle, as it is not only deliquescent, but decomposes more or less in contact with the carbon dioxide which air contains.

S.—Freely soluble in water, feebly soluble in alcohol.

D.—See Tests for Potassium Salts and for Cyanides.

P.—Potassium carbonate will, if present, remain undissolved on treating the powdered sample with alcohol of spec. grav. 85.

Potassium cyanate will if present dissolve with the cyanide in alcohol, and the solution so obtained will give on dilution with water, and on boiling to drive off all the alcohol, a white precipitate with calcium chloride.

Potassium chloride, sometimes present, is detected by precipitating everything present with an excess of silver nitrate, and then boiling the well-washed precipitate with dilute nitric acid, when, if potassium chloride is present, a white precipitate of silver chloride will remain.

Potassium formate is detected by precipitating as above with an excess of silver nitrate, and then boiling the *filtrate*, which will blacken if the cyanide contains any formate.

Potassium ferrocyanide is detected by acidulating the solution with hydrochloric acid (taking special care not to inhale the poisonous hydrocyanic acid given off), and adding ferric chloride to the acidified solution, when a blue colour will indicate ferrocyanide.

Potassium sulphate is detected by the above solution giving a white precipitate with barium nitrate.

Potassium sulphydrate is detected by the unacidified solution of the cyanide giving a black or brown (instead of a pure white) precipitate with mercuric chloride.

U.—Employed in photography as a fixing agent in the collodion processes. Its use in this connection depends upon the property it possesses of converting the silver haloids into soluble double cyanides, a potassium haloid being simultaneously formed. Thus with silver iodide we get  $2KCn + AgI = AgK(Cn)_2 + KI$ . It is always employed in a rather dilute state, because of its solvent action upon metallic silver—a property turned to account in the reduction of fixed silver prints by its means. Owing to its disintegrating action upon gelatine, it cannot be employed as a fixing agent for silver haloids embedded in that substance.

Potassium cyanide is intensely poisonous, both when introduced into the stomach and when absorbed by cuts or abrasions existing on the hands. If any unpleasant effects arise from its absorption through a cut, cotton wool, moistened with chlorine water (q.v.), should be applied to the affected part, a tumbler of water containing half a drachm of that substance being meanwhile drunk, followed by a cup of strong tea or coffee containing brandy.

The symptoms of poisoning by cyanide introduced into the stomach are salty and frothy saliva, general languor, bleeding from the nose and rush of blood to the head, accompanied by temporary blindness and followed by giddiness.

The only reliable antidote is a mixture of ferrous sulphate and ferric chloride, which should be kept in readiness whenever cyanide is used, and is made up as follows:—Into a two ounce bottle put 20 grains of potassium carbonate, and fill up with water, and into another put two drachms of the pharmaceutical tincture of perchloride of iron (Tinctura ferri perchloridi), and half fill with water. At time of using, dissolve 10 grains ferrous sulphate in a little water, add this to contents of second bottle, mix both bottles, and drink off at once, and, after half-an-hour or less, follow this by an emetic, say by 10 grains of powdered Indian tobacco (Lobelia inflata), procurable from any druggist. Failing the powder, a few of the seeds may be used instead. These may be procured at most seed shops.

#### Potassio-ferrous Oxalate.—FeC<sub>2</sub>O<sub>4</sub>·K<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.

The orange liquid obtained by mixing solutions of ferrous sulphate and potassium oxalate contains this substance mixed with potassium sulphate.

L.—It can be obtained pure by dissolving solid ferrous oxalate to saturation in potassium oxalate, mixing this solution with an equal volume of alcohol, and permitting the whole to stand in a stoppered bottle for 24 hours.

U.—An energetic deoxidising agent, and employed for that reason as a dry plate developer (vide Ferrous Oxalate).

## Potassio-ferric Oxalate.—Fe<sub>2</sub> (C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·3K<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.

The greenish substance which crystallises out from spent ferrous oxalate developers, and mixed with potassium oxalate from old hot bath patinotype developers.

- C.L.—Prepared in a pure state by dissolving ferric hydroxide to saturation in acid potassium oxalate (salt of sorrel), and evaporating down the solution.
- A.—Occurs in apple-green tabular crystals, which effloresce in air (the pure variety containing six molecules of water of crystallisation), and gradually becomes brown and opaque on exposure to light.
- S.--Soluble in four parts boiling and sixteeen parts cold water, insoluble in alcohol.
- D.—See Tests for Salts of Iron, for Salts of Potassium, and for Oxalates.
- U.—Employed in certain "blue" processes, owing to the fact that it decomposes under the influence of light, similarly to ferric oxalate (q.v.)

#### Potassium Ferrocyanide.—K<sub>4</sub>Fe(Cu)<sub>6</sub>+3H<sub>2</sub>O

Syn., Ferrocyanide of Potassium, Yellow Prussiate of Potash.

C.—Made by melting 80lbs. of dried potassium carbonate in a cast iron pot provided with a stirrer with 6lbs. of iron borings or clippings, and 100lbs. of nitrogenous matter, of which dried blood and feathers are considered the best, and after these horn clippings, wool, hair, and leather parings.

The potassium carbonate is melted first, then the iron is added to it, and lastly the nitrogenous matter in small quantities at a time, and the mass is kept melted with constant stirring until the smell of ammonia is perceived. When this occurs the mouth of the vessel is tightly closed, and after two hours the contents are broken up, redissolved in water, filtered, and the salt crystallised out. The ultimate change may be roughly represented thus,  $2K_2CO_3+3N_2+Fe+10C=K_4Fe(Cn)_6+6CO$ .

- L.—The commercial salt may be purified by repeated recrystallisation.
  - A.—Occurs in large yellow pyramidal crystals.
- S.—Soluble in twice its weight of boiling and four times its weight of cold water.
  - D.—See Tests for Ferrocyanides and for Potassium Salts.
- E.—Employed in certain "blue" processes and as a test for ferric salts, both of which functions it fulfils, owing to the fact that it changes the colour of such salts to a deep blue. If the ferrocyanide is in excess, the blue substance consists of soluble Prussian blue or potassio-ferric ferrocyanide formed (taking ferric

chloride as the type of a ferric salt) in accordance with the equation  $Fe_2Cl_6+2K_4Fe_1Cn)_6=K_2Fe_2Fe(Cn)_6+6KCl$ . If the ferric salt is in excess the blue substance consists of insoluble Prussian blue or ferric ferrocyanide formed thus,  $2Fe_2Cl_6+3K_4Fe(Cn)_6=Fe_4\{Fe(Cn)_6\}_3^+12KCl$ .

Potassium Carbonate.— $K_2CO_3 + 3H_2O$  or  $K_2CO_3 + H_2O$ , the former if air-dried, the latter if dried at  $100^{\circ}$  C.

Syn., Potashes, Pearlash, Carbonate of Potash.

C.—Prepared commercially from—(1) Plant ashes; (2) carnallite; (3) suint; (4) vinasses.

- (1.) Land plants contain potassium as sulphate and chloride, and in combination with oxalic, malic, tartaric, and other vegetable acids. When the plant is burnt the inorganic potassium salts remain unchanged, but the organic ones become converted into potassium carbonate. To obtain the latter in a comparatively pure state, the ashes are treated with water and a little lime, and the solution filtered and evaporated to dryness, when "potashes" are obtained. "Pearlash" is made by calcining this to remove tarry matters, re-dissolving the residue in water and re-crystallising the salt. The manufacture of potassium carbonate from wood ashes is carried on in America, Russia, France, Belgium, and Austria, and at least half the potassium carbonate of commerce is obtained from this source.
- (2.) Carnallite is a double chloride of potassium and magnesium, approximately represented by the formula KCl·MgCl<sub>2</sub>·6H<sub>2</sub>O, and potassium carbonate is made from it by a process similar to the one employed to make sodium carbonate (q.v.) from common salt. Kainite, a mineral, corresponding to the formula K<sub>2</sub>SO<sub>4</sub>·MgCl<sub>2</sub>·6H<sub>2</sub>O, is also utilised for the same purpose.
- (3.) Suint is the name given to the sweat exuded by sheep and retained in the wool. It contains potassium in combination with certain animal acids, and, by treatment with water, these potassium salts are dissolved, and converted by calcination into potassium carbonate.
- (4.) In the manufacture of sugar from beet, the uncrystallisable molasses are mixed with yeast and fermented, and the alcohol distilled off. The residues technically called "vinasses" are mixed with chalk, when the potassium (present in this case as sulphate) becomes converted into calcium sulphate, which is precipitated, and potassium carbonate, which is obtained in the solid state by evaporating cown the clear liquid.

L.—On a small scale potassium carbonate may be conveniently obtained by calcining cream of tartar (potassium hydrotartrate KHC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>) which, when strongly heated, decomposes into charcoal, potassium carbonate and other products. The black residue so obtained is boiled with water, and the filtered solution evaporated to dryness when the potassium carbonate remains

behind. Another convenient process consists in throwing into a red hot crucible, in small quantities at a time, an intimate mixture of one part of nitre and two parts of oxalic acid, both finely powdered.

Commercial potassium carbonate may be purified by passing carbon dioxide gas into a saturated aqueous solution of it, when potassium hydrocarbonate will separate out. This is collected on a filter, washed with a little water, and then dried and heated to redness, when carbon dioxide escapes, and pure potassium carbonate remains.

- A.—Occurs as a white, deliquescent powder.
- S.—Very soluble in water, insoluble in alcohol.
- D.—See Tests for Potassium Salts and for Carbonates.
- P.—A solution of the salt acidified with nitric acid should give no precipitate with either barium nitrate or silver nitrate, denoting absence of sulphates and chlorides.

U.—Employed in alkaline development and for a variety of

minor purposes.

# Potassium Ferricyanide.—K<sub>6</sub>Fe<sub>2</sub>(CN)<sub>12</sub>.

Syn., Ferrideyanide of Potash, Red Prussiate of Potash.

- C.—Made by passing chloride gas over dry, finely-powdered potassium ferrocyanide spread upon wooden shelves in a closed chamber. The chlorine converts the ferrocyanide into a mixture of ferricyanide and chloride, thus,  $4K_4Fe(CN)_6 + 2Cl_2 = K_6Fe_2(CN)_{12} + 4KCl$ . The orange powder so obtained is dissolved in water, and the solution evaporated down when the less soluble ferricyanide separates out.
- L.—On a small scale the process may be conveniently carried out by adding bromine in small quantities at a time to a strong solution of potassium ferrocyanide, continuing the addition until the solution ceases to give a blue precipitate with ferric chloride. On evaporating down the liquid to half its bulk the ferricyanide will crystallise out, the potassium bromide formed as a result of the reaction remaining in solution. Nitric acid, cautiously added, will bring about a similar change.
  - A.—Occurs in small, red crystals.
- S.—Freely soluble in water, yielding a solution which, under the combined influence of light and air, slowly changes into potassium ferrocyanide and deposits a blue precipitate.
  - D.—See Tests for Ferricyanides and Potassium Salts.
- U.—Employed in certain "blue" processes, owing to the fact that it yields with ferric salts a deep blue precipitate of Turnbull's blue or ferrous ferricyanide. Taking ferrous oxalate as type of a ferrous salt, the action may be represented by  $3\text{FeC}_2O_4 + K_6\text{Fe}_2(\text{CN})_{12} = 3K_2C_2O_4 + \text{Fe}_3\text{Fe}_2(\text{CN})_{12}$ . It is also used mixed with sodium thiosulphate (hypo) as a reducer for too dense negatives or prints. In this case the action is two-fold, the

potassium ferricyanide first converting the silver into silver ferrocyanide, itself being converted into potassium ferrocyanide, thus,  $2Ag_2+2K_6Fe_2(CN)_{1,2}=Ag_4Fe(CN)_6+K_4Fe(CN)_6$ , and the silver ferrocyanide being then dissolved by the hypo, thus,  $Ag_4Fe(CN)_6+4Na_2S_2O_3=4AgNaS_2O_3+Na_4Fe(CN)_6$ , sodium ferrocyanide being simultaneously formed.

#### Potassium Hydroxide.-KOH.

Syn., Potassium Hydrate, Caustic Potash.

C.—Prepared by decomposing potassium carbonate with milk of lime and evaporating down the clear liquid. The change is represented by  $K_2CO_3 + Ca(OH)_2 = CaCO_3 + 2KOH$ .

L.—On a small scale a 10°/o solution may be prepared, thus: Dissolve 6 oz. of potassium carbonate, dried at 100°C., in 20 oz. of water, and boil the solution for 15 minutes with 8 oz. of recently slaked lime. Finally, filter through glass wool or asbestos, and make up the clear liquid to 20 oz.

To purify commercial caustic potash it may be dissolved in alcohol, when the impurities will remain behind.

A.—Met with in commerce as white sticks obtained by fusing the substance and casting it in iron moulds. A purer variety occurs in white lumps. Both these are extremely deliquescent and absorb carbon dioxide from the air, on which account the salt must be kept in well-stoppered bottles.

S.—Freely soluble in water and alcohol.

U.—Employed in alkaline development.

## Potassium Iodide.—KI.

Syn., Iodide of Potash.

C.L.—Prepared by the following methods:—

- (1.) By adding iodine to a strong solution of caustic potash until it is slightly coloured, evaporating to dryness, mixing the residue with  $\frac{1}{10}$ th of its weight of finely powdered charcoal, and throwing the mixture, in small quantities at a time, into a red-hot crucible. The black mass so obtained is then treated with water, and the liquid filtered and evaporated down, when potassium iodide will crystallise out. The change takes place in two stages. By adding iodine to caustic potash, potassium iodide and iodate are formed, thus  $6I + 6KOH = 5KI + KIO_3 + 3H_2O$ , and the iodate on ignition with charcoal becomes converted into iodide  $KIO_3 + C_3 = 3CO + KI$ .
- (2.) Ferrous iodide (FeI<sub>2</sub>) is prepared by leaving a mixture of one part iron filings, two parts iodine, and 10 parts water for 24 hours in a warm place, and the solution so obtained, having been filtered, is mixed with a solution of potassium carbonate until a precipitate ceases to form. By this means the ferrous iodide is converted into potassium iodide, ferrous carbonate being precipitated, FeI<sub>2</sub> +  $K_2CO_3 = FeCO_3 + 2KI$ . The liquid filtered from the precipitated carbonate will yield potassium iodide on evaporation.

(3) A solution of barium iodide (BaI<sub>2</sub>) is first prepared thus—A mixture of one part amorphous phosphorus, 40 parts water, and 20 parts iodine is heated on the water bath until colourless, and then mixed with barium carbonate until neutral, and the whole having been permitted to stand for six hours, is filtered from the insoluble barium phosphate. The liquid so obtained is then mixed with a solution of potassium sulphate until this ceases to produce a precipitate, when insoluble barium sulphate is precipitated, and potassium iodide remains in solution,  $\text{BaI}_2 + \text{K}_2\text{SO}_4 = \text{BaSO}_4 + 2\text{KI}$ . Calcium iodide is frequently substituted for barium iodide, but does not yield so pure a product, as calcium sulpha'e, unlike barium sulphate, is sensibly soluble in water.

The commercial product may be purified by dissolving it in strong alcohol, in which potassium carbonate, sulphate and iodate are insoluble, and the filtered solution so obtained will on distillation to recover the alcohol leave pure potassium iodide as a residue.

- A —Occurs in white cubical crystals.
- S.—Soluble in its own weight of boiling water, and in forty times its weight of alcohol.
  - D.-See Tests for Potassium Salts and for Iodides.
- P.—Potassium bromide is detected by mixing a rather dilute solution of the salt with half its volume of strong sulphuric acid, adding manganese peroxide in small quantities at a time, boiling after each addition. When the addition of peroxide fails to liberate any more violet-coloured iodine vapours, some more sulphuric acid and peroxide are added, and the liquid again boiled, when reddish-brown vapours of bromine will be evolved if potassium bromide is present.

Carbonates, iodates and sulphates are detected by barium nitrate, which precipitates them all. On treating the well-washed precipitate with hydrochloric acid, a residue will remain if a sulphate is present.

Potassium iodate is detected by the blue colour produced on adding starch paste and tartaric acid. The presence of potassium carbonate (a common and, photographically, objectionable impurity) is proved by the turbidity produced when a saturated aqueous solution of the salt is mixed with six times its volume of clear lime water.

Potassium chloride is detected by completely precipitating the salt with silver nitrate, washing the precipitate, shaking it up with two drachms of strong ammonia mixed with three ounces of water, and supersaturating the ammoniacal filtrate with nitric acid, when a turbidity will occur if potassium chloride is present.

U.—Employed to obtain silver iodide by bringing the salt in contact with silver nitrate, when the following change occurs—KI + AgNO<sub>3</sub> = AgI + KNO<sub>3</sub>.

### Potassium Nitrate.—KNO<sub>3</sub>.

Syn., Nitrate of Potash, Saltpetre.

C.—Manufactured by the following methods:—

- (1.) From natural Indian saltpetre earths, which contain it as such. These are treated with water, and the clear liquid is evaporated down, first by the sun's rays, and finally by artificial heat. The impure crystals so obtained are imported from Bengal and Oude, and are known as *Grough* saltpetre. One or more recrystallisations serve to purify them.
- (2.) From artificial nitre heaps made by constructing upon an impervious clay floor, and under shelter of some kind, a species of long clay mound, one side of which is vertical and turned (in this country) towards the east, whilst the other facing the west is cut into steps or terraces. In making the mound, limy clay or marl is selected, and is mixed with leaves and small twigs in order to keep the clay as open and porous as possible. The mound, when finished, is moistened from time to time with any species of refuse organic liquid (urine, liquid manure, stable droppings, &c.) These, by putrefying, yield ammonia, and this by the action of the oxygen of the atmosphere, becomes gradually converted into nitric acid, which combines with the lime to form calcium nitrate, thus:  $2NH_3 + CaO + 4O_2 = Ca(NO_3)_2 + 3H_2O$ . After a couple of years a white efflorescence appears on the windward or easterly side, and when this occurs, several inches of soil are removed from that side and treated with water, fresh soil, &c., being added. In the water the calcium nitrate dissolves, and the liquid yields potassium nitrate on mixing it with potassium carbonate, insoluble calcium carbonate being precipitated thus:  $\frac{\text{Ca(NO}_3)_2 + \text{K}_2\text{CO}_3 = \text{CaCO}_3 + 2\text{KNO}_3}{2\text{KNO}_3}$
- (3.) Chilli saltpetre is sodium nitrate, and potassium nitrate is made from it by mixing its solution with one of carnallite (KCl·MgCl<sub>2</sub>), when sodium chloride and potassium and magnesium chlorides are formed, thus:  $3\text{NaNO}_3 + \text{KCl·MgCl}_2 = \text{KNO}_3 + \text{Mg(NO}_3)_2 + 3\text{NaCl}$ . On concentrating the liquid the less soluble potassium nitrate crystallises out.
  - A.—Occurs in white crystalline masses, or in prismatic needles.
- S.—Soluble in half its weight of boiling, and in four times its weight of cold water.
  - D.—See Tests for Potassium Salts and for Nitrates.
- P.—The solution should not be precipitated by either silver pitrate or barium nitrate, denoting the absence of chlorides and sulphates.
- U.—Employed in the manufacture of nitric acid (q.v.), and of pyroxilin (q.v.). For this latter purpose the salt should be free from chlorides.

# Potassium Metabisulphite. $-K_2S_2O_5$ .

Syn., Metabisulphite of Potash, Metabisulphite.

- C.L.—Made by saturating a strong solution of potassium carbonate with sul, hur dioxide gas, and adding absolute alcohol to the liquid, when the salt will separate out in needle-shaped crystals. The first action is the conversion of potassium carbonate into hydro-potassium sulphite; thus,  $K_2CO_3 + 2H_2SO_3 = 2KHSO_3 + H_2O + CO_2$ , and the hydro-potassium sulphite is then deprived of a molecule of water by the alcohol; thus,  $2KHSO_3 = H_2O + K_2S_2O_5$ .
- A.—Occurs in well-formed, clear transparent crystals, usually smelling of sulphur dioxide.
- S.—Soluble in three times its weight of water. Insoluble in alcohol.
  - D.—See Tests for Potassium Salts and for Sulphites.
- P.—The solution treated with an excess of hydrochloric acid should give only a faint precipitate with barium chloride.
- U.—Employed for the same purpose as sodium sulphite, viz., as a preservative of solutions of pyro, eikonogen, quinol, etc.

# Potassium Oxalate.— $C_2K_2O_4 + H_2O$ .

Syn., Oxalate of Potash.

- C.—Prepared commercially by substituting caustic potash for the mixture of caustic potash and caustic soda, employed in making oxalic acid (q.v.) from sawdust.
- L.—On a small scale potassium oxalate may be made by neutralising potassium carbonate with oxalic acid; thus,  $\mathbf{H_2C_2O_4} + \mathbf{K_2CO_3} = \mathbf{K_2C_2O_4} + \mathbf{H_2O} + \mathbf{CO_2}$ . The following method of procedure will be found convenient. Dissolve 15 ozs. of potassium carbonate in 30 ozs. of water, and place the solution in a large basin, and add to it 10 ozs. of crystalline oxalic acid, in small quantities at a time, and stirring well with a glass rod after each addition. When all the acid has been added test the solution with a piece of blotting paper dipped in phenol phthalein (q.v.), and if acid or alkaline, add more potassium carbonate or oxalic until neutral. Finally evaporate down, or if preferred, dilute it with water until it measures 68 ounces, when a 25 per cent. (nearly) solution of potassium oxalate will be obtained.
- A.—Occurs in white opaque, confused by crystalline masses or in powder.
  - S.—Soluble in three times its weight of cold water.
  - D.—See Tests for Oxalates and for Salts of Potassium.
- P.—Sodium oxalate is detected by moistening some of the salt with strong sulphuric acid, evaporating in an open dish to complete dryness, gently igniting until fumes cease to be evolved, again moistening the cold residue with hydrochloric acid, and holding a platinum wire dipped in the mixture in the colourless bunsen flame, which will be turned yellow if sodium is present.

U.—Employed in making potassium ferrous oxalate (q.v.), and for developing platinotypes, which latter purpose it serves owing to its solvent actions upon ferrous oxalate.

Care should be taken in purchasing this oxalate from druggists that potassium binoxalate or salt of sorrel (KHC<sub>2</sub>O<sub>4</sub>) is not substituted for it. This may be distinguished from potassium oxalate by its inferior solubility (1 in 40). In the event of the mistake having been made, salt of sorrel can be converted into the photographically useful oxalate by neutralising it with potassium carbonate thus:  $2KHC_2O_4 + K_2CO_3 = 2K_2C_2O_4 + H_2O + CO_2$ .

# Potassium Permanganate. - K<sub>2</sub>Mn<sub>2</sub>O<sub>4</sub>.

Syn, Permanganate of Potash.

- C.L.—Prepared by intimately mixing four parts manganese peroxide with  $3\frac{1}{2}$  parts finely powdered potassium chlorate, and five parts of potassium hydrate dissolved in a little water. The pasty mass is then dried and heated to dull redness, when the following change occurs, potassium manganate and potassium chloride being formed  $\mathrm{KCiO_3} + 3\mathrm{MnO_2} + 6\mathrm{KOH} = 3\mathrm{K_2MnO_4} + \mathrm{KCl} + 3\mathrm{H_2O}$ . On treating the fused mass with water, potassium manganate dissolves, forming a dark green solution. This is diluted with water, and a current of carbon dioxide gas passed through it until it has become red, owing to its conversion into permanganate  $-3\mathrm{K_2MnO_4} + 2\mathrm{CO_2} = \mathrm{K_2Mn_2O_8} + \mathrm{MnO_2} + 2\mathrm{K_2CO_3}$ . The precipitated manganese peroxide is allowed to settle, and the clear red solution is evaporated down to small bulk, when potassium permanganate crystallises out.
  - A.— Occurs in dark purple needled-shaped crystals.
- S.—Soluble in 16 times its weight of cold water. The purple solution so obtained is sold as "Condy's red fluid."
- D.—The red solution is decolorised by ferrous sulphate or sodium sulphite.
- U.—Employed as a wet plate intensifier, the silver image having been first converted into silver iodide by acting upon it with iodine and potassium iodide. It is also used to improve old wet plate silver baths, which it does probably by oxidising the organic matter they contain.

# Potassium Thiocyanate.—KCNS.

Syn., Potassium Sulphocyanide or Sulphocyanide of Potash.

C. L.—Made by fusing together at a dull red heat a mixture of 32 parts of flour of sulphur and 17 parts of dry potassium carbonate and adding in small quantities at a time 46 parts of dry finely powdered potassium ferrocyanide, when the potassium cyanide (q.v.) formed by the reaction between the ferrocyanide and carbonate combines directly with the sulphur. The heat is kept up until a small sample, taken out on an iron wire, gives a red colour but no blue precipitate with ferric chloride. When this occurs the

temperature is raised and maintained at a bright red heat (the crucible being covered meanwhile) for 15 minutes. The mass is then permitted to cool, extracted with water, the solution carefully neutralised with sulphuric acid and evaporated to dryness. On treating the mass with alcohol pure thiocyanate dissolves out.

- A .- Occurs in colourless crystals.
- S.—Readily soluble in water and in alcohol.
- D.—Give a blood red color with a solution of ferric chloride.
- U.—Employed in certain toning baths. A cold solution has been proposed as a developer for autotype prints, on account of its solvent action upon gelatine. The salt is exceedingly poisonous.

### Potassium Tri-iodide.—KI3.

This substance is said to be present in the deep brown liquid obtained by dissolving iodine in potassium iodide and is employed (followed by cyanide or hypo) as a reducer for plates or prints.

## Potassium Trisulphide.—K2S3.

Syn., Sulphide of Potash, Liver of Sulphur.

- C.L.—Made by fusing in a crucible a mixture of powdered sulphur with four times its weight of dry potassium carbonate. When effervescence ceases, the fused mass is poured out on a slate slab and permitted to solidify, and at once (being highly deliquescent) transferred to a stoppered bottle. The change is represented by  $K_2CO_3 + S_3 = K_2S_3 + CO_2 + O$ , some of the sulphide being oxidised to sulphate.
  - A.—Occurs as a liver-coloured delequescent amorphous mass.
  - S.—Freely soluble in water.
  - D.—See Tests for Sulphides, and for Potassium Salts.
- U.—Employed to precipitate black silver sulphide from old hypo baths. If such baths contain ordinary alum or chrome alum, potassium trisulphide cannot well be employed for this purpose, as aluminium or chromium hydroxide would be precipitated with the silver sulphide. To recover the silver in such cases sulphuretted hydrogen (which is without action upon salts of aluminium or chromium) is passed through the liquid.

### Potassium Salts, Tests for.

Potassium salts, moistened with a drop of hydrochloric acid, and held on a platinum wire in the colourless bunsen flame, colour it violet.

Solutions containing potassium give the following reactions:
(1.) With an excess of tartaric acid, a white crystalline precipitate, the production of which is much facilitated by adding some sodium acetate. (2.) With platinic chloride, a yellow crystalline precipitate. (3.) With silico fluoric acid, a white gelatinous precipitate. (4.) With picric acid, a yellow crystaline precipitate, provided the solution is sufficiently concentrated.

### Pyrogallol -C6H6O3.

Syn, Trihydroxybenzene, pyrogallic acid, pyro.

- C.—Made on a manufacturing scale thus : -
- (1.) By heating gallic acid (q.v.) mixed with three times its weight of water to  $210^{\circ}-220^{\circ}$ C. for half-an-hour in strong iron vessels, completely closed with the exception of a small aperture, when the following change occurs:  $C_7H_6O_5=C_6H_6O_3+CO_2$ . The residue is then boiled with animal charcoal, filtered, evaporated to dryness at  $100^{\circ}$ C., and the brownish crystals so obtained purified by being sublimed in vacuo.
- (2.) By dissolving phenol (carbolic acid, in strong sulphuric acid, and acting upon the liquid with chlorine when chloro-phenol-sulphonic acid is obtained, which by fusion with caustic soda yields pyrogallol and sodium chloride and sodium sulphite, thus:  $C_6H_3ClOHSO_3H + _2NaOH = C_6H_6O_3 + NaCl + NaHSO_3$ .
- (3.) By rassing carbon droxhide over a mixture of phenol and caustic soda heated to 250°C., dissolving the residue in water, and acting upon the solution with hydrochloric acid when salicylic acid is obtained. From this di-iodosalicylic acid is obtained by the action of iodine, and this, on boiling with strong caustic potash yields pyrogallol, thus:  $C_6H_2I_2OH\cdot COOH + 2KOH = C_6H_6O_3 + Co + 2KI$ .
- L.—On a small scale the first method may be practised by heating to about 220°C. in a hard glass retort a mixture of dry gallic acid and finely powdered pumice, passing over the mixture whilst it is being heated a rapid current of dry carbon dioxide gas. By this means the gallic acid is decomposed, and the pyrogallol distils over and collects in the neck of the retort.
- A better process consists in mixing dry gallic acid with two and a half times its weight of glycerine, and heating the mixture to about 200°C until carbon dioxide ceases to escape. Of course, by this method the pyrogallol is obtained mixed with glycerine.
- A.—Occurs in fine, light needle-shaped crystals more or less tufted together.
  - S.—Freely soluble in water and in alcohol.
- D—Ferrous sulphate gives a purplish blue, and ferric chloride a red colour, the latter changing to brown on heating. Lime water gives a violet colour, changing to dirty brown on heating or on standing. Nitrous acid gives a reddish-brown colour, and this latter test is very delicate when carried out as follows: Add to a strong solution of citric acid a little potassium nitrite, and then some of the liquid suspected to contain pyro, when, if the merest trace is present, a brownish-red coloration will be apparent, and if present in any quantity red fumes will escape on slightly warming the solution. Another characteristic and delicate test consists in fusing the substance suspected to contain pyro with ammonium

oxalate, dissolving the fused mass in water, and adding potassium ferricyanide, when, in presence of pyro, a brown precipitate will occur.

P.—Metagallic acid is present in some samples of pyro, which are consequently more or less brown and leave a residue on being treated with water.

U.—In aqueous solution pyrogallol slowly absorbs oxygen and becomes brown, carbon dioxide being evolved, and acetic acid and a brown humus-like body remaining behind. The presence of an alkali much facilitates the reaction, in which case a carbonate and acetate of the alkali are formed. It will be seen from this that pyro is a deoxidising agent, and its use in photography depends upon this fact. When mixed with silver nitrate (wet plate development) metallic silver is precipitated, and when mixed with the reduction products of the silver haloids (so-called alkaline development) these are attacked.

The brown humus-like body formed during oxidation is bleached by sulphurous acid and by sodium sulphite, for which reason these substances are frequently used in conjunction with pyro to prevent the brown substance from staining the gelatine of the plates. It is doubtful if sulphurous acid or the sulphites actually prevent the slow oxidation of an aqueous solution of pyrogallol: they certainly prevent it from becoming discoloured, but that is quite another matter. The humus-like body formed during development stains the fingers badly, but such stains are easily removed by a mixture of bleaching lime and citric acid.

Pyrogallol is more or less poisonous, four grains having been known to kill a dog. It appears to act by preventing the natural oxidation of the tissures by itself absorbing oxygen from them. The symptoms of poisoning by it are suffocation, accompanied by intense pain in the chest. Potassium chlorate accompanied by stimulants is said to be the best antidote.

# Pyroxilin.

The term employed to denote a more or less nitrated cellulose, soluble in alcohol-ether. Five definite chemical compounds are obtainable by the action of nitric acid upon cellulose, the particular compound formed depending upon the degree of concentration of the acid, the temperature at which the reaction takes place, and the time during which the substances are left in contact.

These compounds are, chemically speaking, nitric ethers of cellulose or cellulo-nitrins, i.e., compounds in which two or more of the hydroxyl (OH) radicles of cellulose have been replaced by oxygen and nitroxyl ( $O_2N$ ) radicles. There is good reason for believing that in these compounds, at least six molecules of cellulose enter, for which reason the generic formula for cellulose ( $C_6H_{10}O_5$ )n is generally written  $C_{36}H_{60}O_{30}$ , or  $C_{36}H_{42}O_{12}(OH)_{18}$ .

By complete replacement of the hydroxyl, we get cellulo-hexanitrin  $C_{36}O_{42}O_{12}$  (ONO<sub>2</sub>)<sub>18</sub>, and by a lesser degree of replacement we get one or other of the compounds tabulated below.

	Cellulose	$C_{36}H_{42}O_{12}(OH)_{18}$
1.	Cellulo-mononitrin	$C_{36}H_{42}O_{12}(OH)_{15}(ONO_2)_3$
2.	Cellulo-dinitrin	$C_{36}H_{42}O_{12}(OH)_{12}(ONO_{2})_{6}$
3.	Cellulo-trinitrin	$C_{36}H_{42}O_{12}(OH)_9(ONO_2)_9$
4.	Cellulo-tetratritrin	$C_{36}H_{42}O_{12}(OH)_6(ONO_2)_{12}$
5.	Cellulo-pentanitrin	$C_{36}H_{42}O_{12}(OH)_3(ONO_2)_{15}$
6.	Cellulo-hexanitrin	$C_{\alpha\alpha}H_{4\alpha}O_{4\alpha}(ONO_{\alpha})_{4\alpha}$

A generic equation representing the reactions can be written thus,  $C_{36}H_{42}(OH)_{18} + nHONO_2 = C_{36}H_{42}O_{12}(OH)_{18} - n(ONO_2)n + nH_2O$ , in which n represents the multipliers 3, 6, 9, 12, 15 or 18.

#### Cellulo-Hexanitrin.

Explosive or gun cotton is made by immersing cellulose (q.v.) in a mixture of 3 volumes of strong sulphuric acid (1.845) and 1, volume of fuming nitric acid (1.52) cooled down to 10°C. and permitting the mixture to act upon the cotton for 24 hours. Another method of preparation consists in taking equal volumes of the same acids, cooling the mixture to 0°C. and immersing the cotton in it for fifteen minutes.

Even when most carefully prepared by either of these methods cellulo-hexanitrin always contains varying quantities of the less nitrated products, but these can be removed by digesting the product with a mixture of 3 volumes anhydrous ether and 1 volume absolute alcohol in which all the cellulo-nitrins but the hexanitrin are soluble.

Cellulo-hexanitrin possesses the original structure of the cellulose, is inflammable, explosive and insoluble in ether, alcohol, ether-alcohol, acetic acid and acetic ether. Acted upon by diluted sulphuric and nitric acids it is more or less denitrated.

## Cellulo-Pentanitrin

is obtained by acting upon cellulose at a temperature of 60°-70°C. for 15 minutes with sulphuric acid (1.845) mixed with half its volume of nitric acid (1.42) or by leaving the cellulose in contact with a mixture of equal volumes of the above acids for about two hours. If the acids are too dilute the tetranitrin will predominate, whilst if too concentrated much hexanitrin will be formed.

Cellulo-pentanitrin is completely soluble in ether, and in etheralcohol provided the alcohol is absolute. If any of it is formed during the conversion of cellulose into photographic pyroxilin, this will give a thick collodion, not very unsuitable for iodising, but good for enamelling purposes.

#### Cellulo-Tetranitrin and Cellulo-Trinitrin

are always formed together in the manufacture of pyroxilin or collodion cotton. The following will, if *implici ly followed*, yield collodion cotton of excellent quality.

Collodion Cotton for wet process:-

Nitric acid (1·45) .. .. 4 ,,

Distilled water.. .. .. 17 drachms

Sea Islands cotton, carded and

thoroughly dried at 120° 130° C... 270 grains

Temperature .. .. .. 67° C.

Times of immersion . . . . 10 minutes.

Nitric acid of the proper strength can be conveniently made by mixing 3 volumes of fuming commercial nitric acid (1.52) with 5 volumes of double aquafortis (1.42).

To make the collodion cotton, wash out a mortar with boiling water, dry it, and place it on the kitchen hob, or on a warm sand bath. Measure out the sulphuric acid into the mortar, add the water in small quantities at a time, and when the temperature has fallen to 67° C., but not before, add the nitric acid also in small quantities at a time, and finally immerse the cotton in 10 grain pieces.

For dry processes the quantity of water should be reduced to 12 drachms, and the temperature raised to 74° C., when collodion cotton yielding a powdery film will be obtained.

The residue of acid left from the first process may be worked up by putting as much cotton in it as it will hold, and leaving the whole for 12 hours in a warm place, when collodion cotton yielding a horny film will be obtained, quite useless for iodising, but excellent for making enamel collodion.

Another method which succeeds well for making collodion cotton is to use a mixture of potassium nitrate and sulphuric acid as follows: Mix six fluid ounces of sulphuric acid (1:845) with a fluid ounce of water, and when the mixture has cooled down to about 70°C. add an ounce of finely-powdered pure potassium nitrate, previously thoroughly dried by heating it to incipient fusion on an iron plate. Stir up with a glass rod, and immerse in this for ten minutes 200 grains of dried cotton. It appears almost impossible to form cellulo-hexanitrate, when a mixture of sulphuric acid and potassium nitrate is used, and the cotton so prepared is in consequence very soluble; but, on the other hand, it gives a film not sufficiently powdery for dry processes.

An open water bath for heating the acid mixture is to be avoided, or failure will probably result, owing to the absorption of steam by the sulphuric acid and the consequent dilution of the mixture.

When the cotton has been in the acids for the proper time it i removed, pressed with a glass rod against the side of the vessel to

drain off as much acid as possible, and then transferred to a large quantity of water, beneath the surface of which it is at once opened out with the fingers, otherwise the temperature may rise sufficiently to cause the cotton to dissolve. The collodion-cotton must be finally well washed in running water for twelve hours, and then air-dried.

Cellulo-tetranitrin is insoluble in absolute alcohol or anhydrous ether, slightly soluble in acetic acid, very soluble in alcohol-ether, in acetic ether, and in alcohol or ether containing water.

Cellulo-tetranitrin is soluble in absolute alcohol, and in acetic acid.

Photographic pyroxilin retains little of the structure of the original cotton, breaks readily, and feels harsh to the touch.

A very pure variety of collodion cotton, known as Schering's Celloïdin, is sold by most dealers, and is suitable for every purpose. It occurs in horny, faintly yellow masses, soluble after twenty-four hours or more in alcohol-ether, yielding collodion giving a perfectly structureless and even film.

On a small scale purified pyroxilin may be made by dissolving 350 grains of collodion-cotton in a pint of strong methylated alcohol, mixed with the same quantity of methylated ether, and then mixing the whole with 10 pints of water and shaking well, when the greater part of the pyroxilin will be reprecipitated. The alcohol-ether can, of course, be recovered by distillation.

### Papyroxilin

Is prepared by using paper instead of cotton-wool, and there are certain advantages in this, as paper is cheaper than cotton, carries no air into the acids, is more easily washed, and less bulky; and changes in temperature during manufacture do not appear to affect the final result to such an extent as with cotton.

Papyroxilin can be easily prepared by immersing fine white unsized paper (Papier Josef, or Swedish filtering paper, answer well) in a mixture of equal volumes of nitric acid (1·42) and sulphuric acid (1·845), cooled to 66°C., leaving the paper in the mixture for twelve hours, or until the paper becomes completely soluble in equal volumes of alcohol and ether. 1lb. of sulphuric acid, and \$\frac{4}{5}\text{lb.}\$ of nitric acid will suffice for 20x. of paper Failing the kinds of paper specified, any kind of good white paper may be used by removing the sizing by soaking it in strong hydrochloric acid for twenty-four hours and then well washing it.

#### Cellulo-Dinitrin

is made by using dilute and hot acids, and is the product often accidentally formed in experiments on the manufacture of collodion cotton, when it is seen that the cotton begins to disintegrate more or less. This cellulo-nitrin is also soluble in ether-alcohol, but gives an opaque film, quite useless for photographic purposes. It is, however, present in the pyroxilin made for manufacturing celluloid.

Celluloid is made by dissolving cellulo-dinitrin mixed with varying quantities of the higher nitrates in wood naphtha or benzol containing some camphor, this latter substance possessing the property of enabling a larger quantity of the nitrated cotton to be taken up. The solution is then heated to expel the solvent, and the residue powerfully compressed and rolled, whilst still warm, into thin sheets. To remove the camphor the sheets are finally treated with carbon disulphide. It does not appear, however, that the camphor is completely removed from most samples of this substance.

Celluloid is plastic and malleable between 120° and 130°C., but very hard and tough at lower temperatures. It has been used for many years as a substitute for ivory for piano and organ keys, billiard balls, etc., and has recently been employed with signal success as a support for the sensitive film of gelatino-bromide of silver. As it is only from ½ to ½ the weight of glass—being besides almost unbreakable—it possesses great and real advantages over this latter substance, and being quite incapable of absorbing water, it is far more convenient than films of insoluble gelatine, which swell more or less in that liquid, and demand special precautions in drying.

# Quinol.— $C_6H_4(OH)_2$ .

Syn., Dihydroxybenzene, Hydroquinone.

C.L.—Prepared by gradually adding two and a-half parts of finely-powdered potassium bichromate to one part of aniline, dissolved in eight parts sulphuric acid, diluted with 30 parts water, when the following change occurs:  $2K_2Cr_2O_7 + 13H_2SO_4 + 6C_6H_5NH_2 = 4KHSO_4 + 2Cr_2(SO_4)_3 + 6C_6H_4(OH)_2 + 3(NH_4)_2SO_4 + 2H_2O$ . Sodium sulphite is next mixed with the brown liquid until it is nearly decolorised, and the mixture shaken up with ether, which dissolves out the quinol. On subjecting the ethereal layer to distillation, the ether is recovered and quinol remains behind.

A.—Occurs as a nearly white crystalline powder, having a sweetish taste.

S.—Soluble in water and in alcohol.

D.—The aqueous solution is turned green by ferric-chloride, and deep red by ammonia, by which reactions quinol may be distinguished from its isomerides, resorcin, and catechol (q.v.)

U.—It is, like pyrogallol, a deoxidising agent, and is on that account employed for similar purposes.

According to Eder, quinol deteriorates after some time, even when dry, such change being unaccompanied by any change of colour.

Quinolin Red.— $C_{26}H_{19}N_2Cl$ .

C.L.—Prepared by heating a mixture of quinolin, zinc chloride, and benzoyl-trichloride to 130° C., or by substituting for the quinolin a mixture in molecular proportions of quinolin and chinaldin.

- A.—Occurs as a deep crimson powder, or in reddish-brown glistening prisms.
- S.—Feebly soluble in water, freely soluble in water yielding a solution with a reddish yellow fluorescence.
- D.—Warmed with sulphuric acid it is bleached, the colour being transiently restored by alcohol.
- U.—Occurs mixed with cyanin blue in commercial azalin (q.v.) used in orthochromatic work.

### Resorcin.—C6H4(OH2.

- C.L.—Prepared by adding four parts of benzol to 15 parts of fuming sulphuric acid, gently heating the liquid for some hours, then evaporating to dryness and heating the residue to  $275^{\circ}\text{C}$ , when benzene disulphonic acid is formed thus:  $\text{C}_6\text{H}_6+2\text{H}_2\text{SO}_4=\text{C}_6\text{H}_4$  (SO\_2OH)\_2+2H\_2O. This is dissolved in water neutralised with lime, the calcium sulphate filtered off, the solution mixed with sodium carbonate, when the calcium benzene disulphonate formed by the excess of lime is converted into sodium benzene disulphonate, and calcium carbonate. This latter is filtered off and the sodium salt fused with two-and-a-half times its weight of caustic soda, when sodium sulphite and resorcin are formed thus:  $\text{C}_6\text{H}_4(\text{SO}_2\text{ONa})_2 + 2\,\text{NaOH} = \text{C}_6\text{H}_4(\text{OH})_2 + 2\,\text{Na}_2\text{SO}_3$ . The fused mass is finally dissolved in water and boiled with hydrochloric acid until no more sulphur dioxide escapes. From this liquid the resorcin is extracted by agitation with ether.
  - A.—Occurs in prisms, having a bitter-sweet taste.
  - S.-Soluble in water and in alcohol.
- D.—The aqueous solution gives a violet colour with ferric chloride, and a brown one with ammonia. Fused with phthalic anhydride, the solid becomes converted into fluoresceine (q.v.), detected by dissolving the fused mass in dilute sulphuric acid, and supersaturating with ammonia, when a splendid green fluorescence will be observed.
- U.—Employed for similar purposes as it isomerides quinol and catechol (q.v.)

#### Rosin.

Chemically speaking, this is a mixture of picric, sylvic, colophonic and pimaric acids, having approximately the formula  $C_{20}H_{30}O_{2}$ .

C.—It is the solid residue left after the distillation of crude turpentine (q.v.) To effect this the turpentine is placed in a copper vessel and heated by a steam jacket, when water and other matters are first given off, followed by turpentine. At a suitable time the distillation is stopped, and the hot rosin drawn off, strained, and permitted to solidify. The comparatively pure variety employed in soap making is termed colophony.

- A.—Its quality depends upon that of the crude turpentine which yielded it, and varies from the finest "window glass" to opaque varieties. Its colour ranges from pale amber to black.
- S.—Its solubility in different liquids varies with its source. Thus the rosin of Venice turpentine dissolves easily in alcohol; whilst that got from Canadian or French turpentine is much less soluble.
  - U.—Employed as a constituent of several varnishes.

#### Sandarac.

Syn., Pounce, Gum Juniper, Juniper Resin, Pine Gum.

- C.—The dried-up juice which exudes from the trunk of the callistris quadrivalvis. A native of America, Africa and Australia.
- A.—A semi-transparent brittle resin, occurring in pale yellow or reddish brown tears, the better varieties of which are nearly transparent.
  - S.—Freely soluble in alcohol, ether and benzol.
- U.—Employed mixed with shellac in varnish making. In quantities not exceeding five per cent of the whole, it gives the varnish an even surface. Larger quantities make varnish too soft to be of much use.

#### Shellac.

Syn., Lac, Gum Lac, Sticklac, Seedlac, Button Lac.

C.—In its crude state of *sticklac* this consists of twigs and small pieces of wood covered by the resinous incrustation deposited by the female lac insect (*Coccus Lacca*) and serving apparently as a protection for her progeny.

To prepare \*eedlac this is passed under rollers, when it peels off from the wood, and the product is then coarsely ground and well washed.

Shellac is made from seedlac by melting and straining it and then casting it into thin sheets, which are finally broken up into small pieces. Of this variety several grades are met with in commerce, the best being known as "fine orange."

Button lac is obtained by melting seedlac and casting it into sticks.

Shellac is purified and freed from wax by dissolving it in a boiling solution of sodium carbonate and reprecipitating it by sulphuric acid.

Bleached lac is prepared by dissolving shellac in caustic soda and passing chlorine through the liquid, when it gradually precipitates as a brownish-white gummy mass, which is then melted and kneaded under repeatedly renewed warm water to free it from chlorine, and finally melted and cast into sticks. This variety of lac should be preserved under water, as in air it rapidly changes and becomes insoluble in alcohol; but when in this condition it can be utilised

by redissolving it in caustic soda and repeating the bleaching process. Another process for bleaching lac consists in boiling 25 parts of shellac in 600 parts of water containing 10 parts of sodium carbonate until dissolved, and mixing this solution, first with  $\frac{1}{20}$ th of its volume of a saturated aqueous solution of calcium hypochlorite (bleaching lime), and then with sufficient hydrochloric acid to completely redissolve the precipitate which is first formed. After letting the solution stand in sunlight for a week or more, it is mixed first with  $\frac{1}{10}$ th of its volume of a saturated aqueous solution of sodium sulphate (Glauber's salt), and then with sufficiently sulphuric acid to precipitate the lac. The precipitate is finally well washed in boiling water and stored in the usual way.

A.—Shellac occurs in reddish-brown, brittle, fusible and inflammable fragments of thin sheets. Bleached lac in white, opague, brittle masses, which should not be glossy on the outside, as this denotes more or less change, and consequent insolubility (vide supra).

S.—All varieties of lac are soluble in alcohol, the solution being facilitated by the addition of oil of lavender. Lac is also soluble in water containing caustic soda, ammonia, carbonate of soda or borax.

U.—Employed as a varnish. A pure alcoholic solution is not very suitable for this purpose, owing to its drying in ridges, which often become cracks, but this is perfectly remedied by the addition of 5% of sandarac. To clear alcoholic solutions, it has been recommended to skake them up with petroleum ether (benzoline), but it is doubtful if this is a good plan, as it removes the wax which confers elasticity upon the shellac, besides introducing benzoline into the varnish. The addition of ammonia to an alcoholic solution of shellac will render the latter mixable in all proportions with water.

To make an aqueous ammoniacal solution of shellac, boil the latter with a quantity of water just sufficient to cover it, and add ammonia in a then stream, stirring constantly until dissolved and taking care to add no more than is absolutely necessary, otherwise the solution will blacken very considerably.

## Silver.—Ag.

A metal occurring native either alone or associated with iron, mercury, copper, platinum, and gold, and with various non-metallic elements. Its chief ores are:—

(1.) Silver glance or silver sulphide (Ag<sub>2</sub>S), the richest source of silver. (2.) Stephanite (5Ag<sub>2</sub>S.Sb<sub>2</sub>S<sub>3</sub>), an antimonial silver sulphide. (3.) Pyrargyrite (3Ag<sub>2</sub>S.Sb<sub>2</sub>S<sub>3</sub>), or ruby silver ore. (4) Antimonial silver. (5) Proustite (3Ag<sub>2</sub>S,As<sub>2</sub>S<sub>3</sub>), an arsenical silver sulphite. (6) Stroneyrite (Ag<sub>2</sub>S.Cu<sub>2</sub>S). (7.) Fahl ore, a mineral consisting of sulphides of silver, copper, iron, tin, lead, and mercury. (8.) Hornsilver (AgCl), a native silver chloride. (9)

Bromargyrite (AgBr). (10.) Iodargyrite (AgI). (11) Amalgam silver, a mixture in variable proportions of silver and mercury. (12.) Argentiferous galena, or lead sulphide (PbS), containing variable quantities of silver sulphide.

- Of these ores, silver glance, stephanite, and pyrargyrite are found chiefly in Saxony, Bohemia, Mexico, and Chilli, antimonial silver in the French Dauphiné, proustite in the Duchy of Baden Baden, fahl ore in Sweden, and amalgam silver in the Palatinate, whilst the British Islands furnish galena, pyrargyrite and fahl ore, the latter in small quantities Owing to the high price of silver, and the comparative facility with which it may be extracted from its ores, this extraction is profitable, even when the ore contains a mere trace of silver. Thus the Mexican ores contain as a rule only '25% of silver, and are considered rich when the percentage of metal rises to '5%. The ores worked at Clausthal, in the Hartz, contain only about '1% of silver, and the Freibergh ores only '05%, and the extraction of siver from argentiferous galena is profitable even when the percentage of metal does not exceed '01%.
- C.—The various methods in use for the extraction of silver from its ores may be divided into three classes:—
- (1) Amalgamation methods as employed at Freiberg and in Mexico, and based upon the solubility of silver in metallic mercury, and the ready volatilisation of the latter by heat.
- (2.) Wet methods, chiefly used in Saxony and Hungary, by which the ore is first converted into a compound soluble in water, or a solution of some suitable salt, from which solution the silver is subsequently recovered by precipitation.
- (3) Concentration methods, by which all the silver is dissolved in molten lead, and subsequently recovered by cupellation or oxidation of the lead.
- (1.) The amalgamation process is carried out in Mexico by finely grinding the picked ore, and mixing it with water, common salt, and an impure copper sulphate obtained by roasting copper pyrites. The mixture is then trodden on by horses or mules for a considerable time, having been placed for that purpose in a water tight pit. The common salt appears to convert the silver sulphide into chloride, and this in contact with the metallic mercury yields mercurous chloride and metallic silver, thus, 2AgCl + Hg<sub>2</sub> = Hg<sub>2</sub>Cl<sub>2</sub> + Ag<sub>2</sub>. Finally, more mercury is squirted over the surface of the mass, and the whole, after having been again well trodden on, is transferred to a tank of running water, which partly dissolves and partly carries away the extraneous matters, leaving behind an amalgam of silver and mercury. This is then strongly heated, when the mercury escapes, and is condensed. and metallic silver remains behind. At Freiberg the ore is roasted with common salt and copper pyrites, and the finely ground mixture is then introduced into revolving barrels containing mercury, which after some time amalgamates with the silver. The subsequent processes resemble those used in Mexico.

(2.) The wet methods of extracting silver from its ores being simpler and less costly than the older amalgamation methods have to a great extent supplanted them, at least in Europe. They may be conveniently classified into—

(a.) Augustin's process, practised in Saxony and Hungary, in which the silver chloride, formed by roasting the finely-ground ore with common salt, is dissolved out by means of a concentrated solution of the same substance. From this solution metallic silver is precipitated, by permitting metallic copper to act upon it, cuprous chloride being formed thus,  $2AgCl + Cu_2 = Cu_2Cl_2 + Ag_2$ .

(b.) Ziervogel's process, used at the great Mansfield works in Hungary, in which, by roasting the argentiferous copper schist (essentially a double sulphide of silver and copper), the silver is converted into soluble silver sulphate, and the copper into insoluble copper oxide, thus,  $CuS + Ag_2S + O_7 = Ag_2SO_4 + CuO + SO_2$ . The mixture is then treated with water, in which the silver sulphate dissolves, and from this solution the silver is precipitated by acting upon it with metallic copper. A somewhat similar process is adopted at Swansea.

(c.) Von Patera's process, employed in Bohemia and elsewhere, in which the silver is converted as in Augustin's process into silver chloride, which is then dissolved out by sodium thiosulphate (hypo), and from this the silver is precipitated as sulphide by the action of sodium sulphide, and this, on being strongly heated,

decomposes into sulphur dioxide gas and metallic silver.

(3.) Concentration methods, which are applied either to bring about the concentration of ores containing traces of silver, as in Norway, by fusing them with lead, or, as in England, to the desilverisation of argentiferous lead obtained from galena. To carry out the process the silver is first concentrated in a small quantity of lead by melting the alloy, permitting it to cool down somewhat, and ladling out the portions which solidify first, and which contain nearly all the lead. The residue is then transferred to a reverberatory furnace having a bed of bone-ash, and strongly heated in a current of air. The lead under these circumstances oxidises to lead oxide, and this fuses and sinks into the porous bed, finally leaving the silver in the pure condition on the bed of the furnace. The silver obtained by any of these methods contains traces of impurities which render it brittle and unfit for coinage, etc. The silver is purified by melting the silver on a porous furnace bed, and keeping the molten metal well stirred, under which circumstances all the impurities present are either oxidised and volatalised, or absorbed by the porous bed. The operation is continued until a drop of the molten silver, taken out on the point of an iron rod, presents a surface free from tarnish, and assumes on solidification the characteristic properties of pure metallic silver.

A.—Silver is remarkable for its white colour, being, with the exception of iridium, the only purely white metal. In malleability and ductility it ranks next to gold It is, when quite pure, rather softer than gold, but not so soft as lead, and is the best known conductor of heat and of electricity.

Owing to its softness it cannot be employed as such for coinage, etc. To harden it, it is alloyed with copper. Standard British coin contains 92.5% of silver, or 18dwts. of copper per pound troy.

In commerce the purity of silver is referred to this standard, and silver articles are spoken of as so many pennyweights better or worse than it. Thus French coinage containing 24dwts. of copper per lb. troy is spoken of as 6dwts. worse, whilst Indian coinage containing only 12dwts. of copper would be spoken of as 6dwts. better.

All silver goods are, or should be, assayed at offices specially established for that purpose, and the "hall marks" on manufactured articles showing where they have been tested are as follows:—Birmingham, an Anchor; Chester, three wheatsheaves or a dagger; Dublin, a harp or figure of Hibernia; Edinburgh, a thistle or castle and lion; Exeter, a castle with two wings; Glasgow, a tree and a salmon with a ring in his mouth; London, a leopard's head; Newcastle-on-Tyne, three castles; Sheffield, a crown; York, five lions and a cross.

The "standard mark" for silver of the same fineness as British coin is for England a lion, for Scotland a thistle, and for Ireland a harp crowned.

Water at ordinary temperatures and air free from sulphuretted hydrogen are without action upon it, the tarnishing of silver articles being due to the traces of sulphuretted hydrogen which the air contains.

It combines directly with chlorine, bromine, and iodine at ordinary temperatures, such combinations being effected in the Daguerreotype process.

Use is made of the fact that silver combines directly with iodine to remove stains of metallic silver formed on the hands, etc., by silver nitrate (q v). These are first painted over with potassium triodide (q.v.), and the silver iodide formed is then treated with potassium cyanide or hypo, when it at once dissolves. Hypo is, of course, safer to use on the hands than potassium iodide, but not perhaps quite so effective.

S.—Concentrated boiling sulphuric acid converts it into silver sulphate, with the liberation of sulphur dioxide,  $Ag_2 + 2H_2SO_4 = Ag_3SO_4 + 2H_2O + SO_2$ . Hydrochloric acid has little effect upon it unless the metal is very finely divided, when it becomes converted into chloride, hydrogen being liberated thus,  $2Ag + 2HCl = 2AgCl + H_2$ . The chlorides of potassium, sodium, and ammonium effect a similar change with the production of in the case of potassium and sodium the hydroxide of the alkaline metal, thus,  $NaCl + Ag + H_2O = NaOH + H + AgCl$ , whilst with ammonium chloride ammonia is liberated,  $NH_4Cl + Ag = AgCl + NH_3 + H$ . Cupric, ferric, and mercuric chlorides are, on the other hand, reduced by finely-divided silver into cuprous, ferrons, and mercurous chlorides, silver chloride being simultaneously formed. Nitric acid readily attacks it, forming silver nitrate thus,  $6Ag + 8HNO_3 = 6AgNO_3 + 4H_2O + 2NO$ .

#### U.—Employed to manufacture silver nitrate (q.v.)

The following table, due to Mr Thomas Fletcher, of Warrington, may occasionally be found useful: -

#### SILVER COINS.

				-	
Country.	Name of Coin.	Fineness.	Standard Weight.	Weight of Pure Silver.	Va'ue.
England France United States India Austria Prussia	Shilling Franc Dollar Rupee Rix Dollar (1800) Rix Dollar (Convention)	In 12 parts.  11'2  10'15  10'13½  11'0  9'17  9'19	Grains.  93  75  400  178½  384  388	Grains.  86  69½  370  165  355½  359	s. d. 11 <sup>6</sup> / <sub>10</sub> 9 <sup>1</sup> / <sub>10</sub> 4 2 1 10 <sup>1</sup> / <sub>4</sub> 4 0

#### Silver Albuminate.

Syn., Albuminate of Silver.

The name given to the probably indefinite compound formed when albumin is mixed with silver nitrate.

A.—A nearly white insoluble substance, reddened by exposure to light.

U.-Occurs mixed with silver chloride in albuminised paper.

# Silver-ammonio Nitrate.—AgNO32NH3.

Syn., Ammonio-nitrate of Silver.

C.—Prepared by adding ammonia to a solution of silver nitrate until the precipitate first formed is redissolved, AgNO<sub>3</sub> + 2NH<sub>4</sub>OH = AgNO<sub>3</sub>2NH<sub>3</sub> + 2H<sub>2</sub>O.

U.—Employed in solution for sensitising plain paper for positive printing, and for making gelatino - bromide of silver by the ammonia process.

# Silver Bromide.—AgBr.

Syn., Bromide of Silver.

C.L.—Made by the direct union of silver and bromine, as in the Daguerreotype process, or by the double decomposition which ensues when solutions of silver nitrate and any soluble bromide are mixed. It is prepared in this latter way in both collodion and emulsion processes. Taking ammonium bromide as the type of a soluble bromide, the reaction would be  $\mathrm{NH_4Br} + \mathrm{AgNO_3} = \mathrm{AgBr} + \mathrm{NH_4NO_3}$ .

A.—Usually occurs on a yellowish precipitate. According to Stas, it occurs in six distinct physical states, viz.:-

- 1. A white flaky state.
- 2. A yellow flaky state.
- 3. An intense yellow powdery state.
- 4. A pearly white powdery state.
- 5. A yellowish white powdery state. 6. An intense yellow melted state.

The first two are made by mixing cold aqueous solutions of silver nitrate with a soluble bromide, and these can be converted into the third and fourth variety by vigorous agitation with water. Any of the first four varieties become converted into the fifth by being boiled with water, and this modification may also be produced direct by adding a soluble bromide to a dilute boiling solution of silver nitrate. Of these the fifth is the most sensitive to light, and is also more granular than the others, being seen under the microscope to consist of comparatively large particles.

De Pitteurs classifies the photographically useful varieties of silver bromide as follows:-

	By transmitted	By reflected	Photographic occurrence.
Saidanaa	Orange	Slaty-blue Bluish-white	.Very fresh collection emulsions. .Ripened emulsion and
Semi-transparent -	Reddish orange	Bluish-white	wet collodion.  Very sensitive wet collodion.  Very old collo-emulsions
	(	(Yellowish-white.	Very old collo-emulsions
	Violet blue	Greenish-yellow	Freshgelatine emulsions
Almost opaque		Green or Greenish-violet	Ripened gelatine emul-
	Blue	Indistinct	.Red-sensitive gelatine emulsions giving
	\		foggy pictures.

The sensitiveness of silver bromide to light is, like that of the iodide and chloride, greatly increased by the presence of bromine absorbents (sensitisers), and retarded by oxidising agents. Like the other haloid salts of silver, alkaline pyro and kindred substances b'acken it, probably converting it into metallic silver. The action of light upon it has been variously stated to convert it into subbromide Ag, Br, oxybromide Ag, O.2AgBr, or photo salt xAgBr yAg, Br, but the precise change is still a matter of dispute. It appears at all events conceded on all hands that the visible change produced by the long-continued action of light is similar in kind to the invisible change (developable image) produced by short exposure.

S. Insoluble in water and in 5% ammonia. Soluble in strong (a) ammonia, (b) in potassium cyanide, and (c) in sodium thiosulphate, the reactions being represented by-

(a)  $2AgBr + 6NH_4OH = 2 AgBr 3NH_3 + 6H_2O$ .

(b)  $AgBr + 2KCN = KBr + AgK(CN)_2$ . (c)  $AgBr + Na_2S_2O_3$ ,  $= NaBr + AgNaS_2O_3$ .

- D.—A 5% solution of ammonia, in which silver chloride dissolves, serves to distinguish between it and silver bromi'e, and strong ammonia, in which silver iodide is insoluble, dissolves silver bromide fairly well.
  - U.—Employed in wet collodion and in emulsion processes.

#### Silver Chloride.—AgCl.

Syn., Chloride of Silver.

C.L.—Made like silver bromide (q.v.)

A.—A white insoluble substance, changing colour in actinic light, provided water, organic matter, or chlorine absorbents of some kind are present, but said to remain unchanged if quite free from these. The change of colour is prevented by oxidising agents like chlorine, bromine, etc.

By short exposure it becomes converted into a substance capable of forming the nucleus of a developable image, the change being probably similar to that which silver bromide (q.v.) undergoes.

- S.—Faintly soluble in water, freely soluble in ammonia of any strength, and in the solvents of silver bromide (q.v.)
  - D.—See Silver Bromide and Iodide.
  - U.—Employed in printing out processes and in emulsions.

### Silver Cyanide,

Two cyanides of silver are known, the normal insoluble cyanide AgCN and potassio-silver cyanide AgK(CN)<sub>2</sub>, formed by dissolving this in potassium cyanide, or by acting upon any salt of silver with an excess of potassium cyanide.

This double cyanide is present in old cyanide fixing solutions, from which the silver can be precipitated as silver sulphide by potassium trisulphide (q.v.)

# Silver lodide.-AgI.

Syn., Iodide of Silver.

- C.L.—Prepared like the bromide (q.v.) The degree of dilution of the solutions appears to modify the colour of the product, that precipitated from concentrated solutions being deeper in tint than the product got when more dilute solutions are employed.
- A.—A yellow or yellowish-white insoluble substance, acted upon by light like the corresponding bromide or chloride.
- S.—Insoluble in strong ammonia, but whitened by it. If, however, any other haloid salts are present some of the iodide will dissolve, a comparatively soluble double salt being formed. It is also soluble in the solvents for silver bromide  $(q \cdot v)$ .

D.— It may be distinguished from silver bromide or chloride by its insolubility in ammonia, or better by shaking it up with a strong solution of silver nitrate, in which it dissolves, but in which silver chloride or bromide are quite insoluble. The liquid so obtained becomes turbid on boiling or on dilution. Advantage is taken of this fact to separate out the excess of silver iodide present in old collodion baths. Another interesting way of distinguishing silver iodide from the bromide or chloride is to cover it with a little water, and expose the whole to light for a considerable time, when, on testing the water with litmus, it will be found quite neutral. Silver chloride and bromide, similarly treated, liberate chlorine and bromine, which become converted by the water into hydrochloric or hydrobromic acids, manifested by the acid reaction the water yields when tested with litmus.

U.—Employed in collodion work and in emulsions.

# Silver Oxide.—Ag<sub>2</sub>O.

Syn., Oxide of Silver.

C.L.—Obtained as a brown precipitate, when a solution of caustic soda or potash is added to one of silver nitrate, and prepared in the pure state as follows:—Dissolve half an ounce of silver nitrate in four ounces of water, and add the solution to four pints of lime water. When the precipitate has settled to the bottom pour off the liquid without disturbing the precipitate, and fill up again with water. A second decantation will get rid of the last traces of calcium nitrate. The reaction may be represented by  $2AgNO_3 + Ca(OH_2 = Ag_2O + H_2O + Ca(NO_3)_2$ . It is best preserved under water, as if dry and in contact with air it rapidly becomes converted into silver carbonate. Care must be taken not to bring it in contact with ammonia, otherwise the dangerously explosive silver nitride (NAg<sub>3</sub>) or fulminating silver will be formed.

A.—A brownish-black amorphous substance.

S.—Feebly soluble in water, to which it imparts an alkaline reaction.

U.—Employed to neutralise solutions of silver nitrate which, from any cause, have become acid.

### Silver Nitrate.—AgNO<sub>3</sub>.

Syn., Nitrate of Silver, Lunar Caustic.

C.L.—Prepared by dissolving pure silver (q.n.) in nitric acid, evaporating the solution to dryness, gently heating the residue to expel the excess of acid, redissolving it in the smallest possible quantity of water, filtering the solution to separate any nitrite which may have been formed, and recrystallising.

To dissolve the silver, it is best to use the concentrated acid, and to conduct the operation in a flask, so as to avoid loss by spirting.

About two measured ounces of strong nitric acid will be required for every three ounces of silver.

In dissolving up silver containing copper, this latter must be got rid of. This may be effected in two ways. The one most economical of time and material is to convert the copper nitrate into copper oxide by gently fusing the green product obtained on evaporating the solution to dryness until a sample dissolved in water ceases to give a blue coloration when mixed with an excess of ammonia.

A second plan consists in evaporating down the liquid to syrupy consistence and adding strong nitric acid (1·42) in quantity equal to six times the volume of the liquid, when silver nitrate, being almost insoluble in nitric acid of that degree of concentration, will separate out, the copper nitrate being taken up by the acid. The precipitated silver nitrate is finally collected on a filter of glass wool, washed with a little strong nitric acid, dried in a current of hot air, and re-crystallised.

A.— Occurs in colourless tabular crystals, and (as lunar caustic) in translucent sticks. Silver nitrate acts as a powerful caustic, oxidising and destroying the skin and tissues, its action depending upon the facility with which it becomes reduced, in contact with organic matter, to metallic silver. For the same reason solutions containing silver nitrate and organic matter, such as the baths used for sensitising albuminised paper, readily become discoloured. Such discoloration is readily removed by mixing them with a little koalin (q.v.), which in falling to the bottom of the bottle mechanically carries down the finely-divided metallic silver. This action appears to be greatly facilitated by actinic light.

S.—Recrystallised silver nitrate is soluble in its own weight of water, giving a faintly alkaline solution, and in four times its weight of alcohol. The fused nitrate (lunar caustic) gives a milky solution, owing to the presence of silver nitrate, which is, however, rendered clear by the addition of a few drops of nitric acid. Lead, tin, zinc, iron, cadmium, copper, antimony, and phosphorus precipitate metallic silver from solutions of silver nitrate.

D.—See Tests for Nitrates and for Salts of Silver.

P.—To examine a commercial sample of silver nitrate, dissolve it in water, completely precipitate the silver with pure hydrochloric acid, filter and evaporate the filtrate to dryness, when no residue should remain. If there should be any remain ignite it, when white fumes will indicate the presence of ammonium nitrate in the sample. If a residue remain after continued ignition, treat it with boiling water, and test the soluble portion for potassium and sodium in the usual way (vide tests for these salts), when positive results will indicate the presence of potassium or of sodium nitrate. The insoluble portion left after treating the residue with water is dissolved in a little nitric acid diluted with water, and tested for lead with sulphuretted hydrogen, and for magnesium with ammonium hydroxide and sodium phosphate.

U.—Employed for a variety of photographic purposes, in which connection the following table may prove useful:—

EQUIVALENTS IN GRAINS OF 100 GRAINS OF SILVER NITRATE.

NAME.		FORMULA.		GRAINS.
Potass. chloride	 	KCl		44
" bromide	 	KBr		70
" iodide	 	KI		98
Sodium chloride	 	NaCl		34
" bromide	 	NaBr		61
,, iodide	 	NaI		89
Ammonia chloride	 	NH <sub>4</sub> Cl		32
" bromide	 	$NH_4^*Br$		58
" iodide	 	NH <sub>4</sub> I		86
Lithium chloride	 	LiCI		25
" bromide	 	LiBr		51
,, iodide	 	LiI		79
Strontium chloride	 	$SrCl_2 + 6H_2O$		73
,, bromide	 	$SrBr_2$		72
" iodide	 	$SrI_2$		100
Calcium chloride	 	CaCl <sub>2</sub>		33
" bromide	 	$CaBr_2 + 4H_2O$		80
,, iodide	 	CaI,		87
Cadmium chloride	 	CdCl <sub>2</sub>	!	54
" bromide		$CdBr_2 + 4H_2O$		101
,, iodide	 	CdI <sub>2</sub>		108
Magnesium chloride		MgCl <sub>2</sub>		28
,, bromide		MgBr <sub>2</sub>		54
,, iodiđe	 	MgI <sub>2</sub>		82
Zinc chloride	 	ZnCl <sub>2</sub>		40
" bromide	 	$ZnBr_2^2$		66
" iodide				94

Silver nitrate taken internally acts as a corrosive poison, the best antidote being a solution of common salt.

### Silver Nitrite.—AgNO2.

Syn., Nitrite of Silver.

C.L.—Formed by fusing silver nitrate, thus,  $AgNO_3 = AgNO_2 + O$ , or (pure) by mixing solutions of sodium or potassium nitrite and silver nitrate  $KNO_2 + AgNO_3 = KNO_3 + AgNO_2$ .

A —Occurs as a brownish powder.

S.—Feebly soluble in cold water, readily soluble in hot water, and with decomposition in nitric acid.

U.—It is said that the presence of a trace of it in silver baths used in the collodion process conduces to sensitiveness.

## Silver Sodium Thiosulphate.

Syn., Double Hyposulphite of Silver and Sodium.

L.—Two compounds of this name are known. The first is formed when any silver salt is brought in contact with an excess of sodium thiosulphate (hypo), and agrees with the formula  $\operatorname{AgNaS}_2\operatorname{O}_3$ , being formed thus, taking silver bromide as type of a silver salt,  $\operatorname{AgBr} + \operatorname{Na}_2\operatorname{S}_2\operatorname{O}_3 = \operatorname{AgNaS}_2\operatorname{O}_3 + \operatorname{NaBr}$ . This thiosulphate is freely soluble in water, yields an intensely sweet solution, and crystallises in flat plates.

The second compound corresponds to the formula  $Ag_2Na_4(S_2O_3)_3 + 2H_2O$ , and is formed when salts of silver in excess are mixed with sodium thiosulphate. It is a white substance, almost insoluble in water, and readily decomposed into black silver sulphide, sodium thiosulphate and oxygen.

The former salt is present in all hypo fixing baths, from which the silver can be separated as silver sulphide by the action of potassium trisulphide (q.v.) or sulphuretted hydrogen.

#### Silver Sulphide.—Ag<sub>2</sub>S.

Syn., Sulphide of Silver.

L.—Formed by the action of sulphuretted hydrogen, or of an alkaline sulphide upon metallic silver or any of its compounds. It is the form in which silver is recovered from old fixing baths. By fusion either alone or mixed with an alkaline carbonate it becomes converted into metallic silver. In the former case the fusion has to be long continued; in the latter the conversion is complete in a much shorter time.

A.—Occurs as a black solid when in large masses, but brown powder when finely divided.

S.—Insoluble in water, ammonia, cyanide or hypo. Soluble in nitric acid, becoming converted into silver sulphate and nitrate.

## Silver Salts, Tests for

Soluble silver salts give the following reactions:—(1.) With hydrochloric acid a white precipitate soluble in ammonia. (2.) With sulphuretted hydrogen a black precipitate. (3.) With potassium chromate a brick red precipitate. (4.) With sodium or ammonium hydrates a brown precipitate, soluble in latter case in excess (5.) With sodium phosphate a yellow precipitate soluble in ammonia. (6.) With potassium iodide a yellow precipitate insoluble in ammonia. (7.) With potassium bromide a yellowish white precipitate insoluble in 5 % ammonia.

# Sodium Acetate,—NaH<sub>3</sub>C<sub>2</sub>O<sub>2</sub>.

Syn, Acetate of Soda.

C L.—Made by neutralising acetic acid with sodium carbonate,  $2H_4C_2O_2 + Na_2CO_3 = 2NaH_3C_2O_2 + 2H_2O + CO_2$ .

A.—Occurs in small transparent crystals.

- S .- Soluble in water and in alcohol.
- D.—See Tests for Sodium Salts and for Acetates.
- P.—A dilute aqueous solution of it should not be blackened by ammonium sulphide, and should not give precipitates with either silver or barium nitrates.
- U.—Employed in toning (vide gold), for which purpose it should be quite free from chlorides, but the presence of even considerable quantities of sulphates appears to be of little moment.

#### Sodium Bromide -NaBr.

Syn., Bromide of Soda.

C.L.—Prepared like potassium bromide (q.v.).

A.—Occurs in small white crystals.

S.—Fairly soluble in water, and in alcohol.

D.—See Tests for Sodium Salts and for Bromides.

U.—It has been stated on good authority that the use of this salt in preparing gelatine emulsions renders them more sensitive to orange and yellow rays than if potassium or ammonium bromide had been used.

#### Sodium Chloride.-NaCl.

Syn, Chloride of Sodium, Sea Salt, Common Salt, Table Salt, Rock Salt, Sal Gemme, Bay Salt.

C.—Bay Salt is the crude product obtained by the evaporation of sea water, which contains about 3% of sodium chloride. The process is carried out on a small scale at South Shields, and very extensively along the west coast of France and Portugal, the east coast of Spain, and the south-east coast of France.

Rock Salt occurs naturally in beds in Cheshire, Staffordshire, Worcestershire, and in many places on the Continent and in America. Perfectly pure colourless crystalline cubes of it constitute

Sal Gemme, ordinary rock salt, being more or less brown from the presence of iron.

Table Salt is purified rock salt, but still retains traces of many impurities.

L-Pure sodium chloride may be prepared by neutralising pure hydrochloric acid with pure sodium carbonate,  $2 HCl + Na_2CO_3 = 2 NaCl + H_2O + CO_2$ , or by passing a current of hydrochloric acid gas through an aqueous filtered solution of white table salt, when the pure salt crystallises out, being insoluble in strong hydrochloric acid, the impurities (chiefly magnesium chloride) remaining in solution. At the conclusion of the operation the precipitate is collected on a filter of glass wool, washed with a little strong hydrochloric acid, and dried in a current of air.

A —Pure sodium chloride occurs in minute white crystals, which are permanent in air.

- S.—Soluble in three times its weight of cold and twice its weight of hot water. Insoluble in alcohol.
  - D.—See Tests for Sodium Salts, and for Chlorides.
- P.-Pure sodium chloride should give no precipitates with ammonium oxalate, denoting absence of calcium salts, and the filtrate from this precipitate, if any, should give no precipitate with ammonium chloride, ammonium hydrate and sodium phosphate, denoting absence of magnesium. Sulphates are detected by barium nitrate.
- U.—Employed in preparing albuminised paper, and in the manufacture of gelatino-chloride emulsions.

#### Sodium Carbonate.—Na<sub>2</sub>CO<sub>3</sub>.

Syn., Washing Soda, Soda Crystals, Sal. Soda, Carbonate of Soda.

C. - Prepared commercially by five distinct methods: -(1) Leblanc's process: This consists in strongly heating common salt with sulphuric acid in a species of reverberatory furnace, when the following change occurs, 2NaCl+H2SO4=2HCl+Na2SO4. The liberated hydrochloric acid (q.v) is condensed by passing it in o water, and the sodium sulphate, technically known as salt cake, is decomposed by being intensely heated, mixed with limestone and small coal. The latter change may be represented thus, (a)  $Na_2SO_4 + 4C = Na_2S + 4CO$ , (b)  $CaCO_3 + C = 2CO + CaO$ , (c)  $CO + O = CO_2$ , (d)  $Na_2S + CaO + CO_2 = Na_2CO_3 + CaS$ . The residue of calcium sulphide, sodium carbonate, etc., known as black ash is treated with hot water, permitted to settle, and the clear liquid evaporated down, when crude soda ash separates out. To purify this it is incorporated with sawdust, and the whole again strongly heated when on treatment with water soda crystals, commonly called washing soda is obtained. (2.) Hargreaves process: This consists in leading a mixture of steam, air, and sulphur dioxide gas, produced by the combustion of pyrites over common salt, heated to dull redness, when the following change occurs,  $2\text{NaCl} + \text{H}_2\text{O} + \text{SO}_2 + \text{O} = \text{Na}_2\text{SO}_4 + 2\text{HCl}$ . sodium sulphate is then treated as in the Leblanc process. (3.) Deacon's process: This is carried out by passing steam, chlorine, and sulphur dioxide gas over common salt, the latter being made to slide down a series of inclined planes arranged in a strongly heated tower. Under these circumstances the steam, chlorine and sulphur dioxide react to produce hydrochloric and sulphuric acids, thus  $SO_2 + 2H_2O + Cl_2 = 2HCl +$ H<sub>2</sub>SO<sub>4</sub>, the latter then reacting upon the common salt to convert it into sulphate, which is treated as before. (4.) The Solvay or ammonia process: In this process a saturated solution of common salt mixed with one fifth its volume of strong ammonia is decomposed by passing a current of carbon dioxide gas through it thus. (a.) NH<sub>3</sub> + H<sub>2</sub>O + CO<sub>2</sub> = NH<sub>4</sub>HCO<sub>3</sub>. (b.) NaCl + NH<sub>4</sub>HCO<sub>3</sub> = NH<sub>4</sub>Cl + NaHCO<sub>3</sub>, the sodium bicarbonate which is precipitated, being converted into sodium carbonate by strongly heating it  $2NaHCO_3 = H_2O + CO_2 + Na_2CO_3$ . The residual ammonium chloride is heated with magnesia, when ammonia is evolved, thus  $2\mathrm{NH_4Cl} + \mathrm{MgO} = 2\mathrm{NH_3} + \mathrm{H_2O} + \mathrm{MgCl_2}$ , the ammonia being dissolved in water and utilised again, and the magnesium chloride is also utilised by strong heating it when magnesia remains, the liberated hydrochloric acid being condensed in water  $\mathrm{MgCl_2} + \mathrm{H_2O} = \mathrm{MgO} + 2\mathrm{Hcl.}$  (5.) A fifth process consists in decomposing the mineral cryolite (a double fluoride of aluminium and sodium represented by the formula  $\mathrm{Na_3AlF_6}$ ) with slaked lime.

- A.—We may classify the commercially procurable varieties of sodium carbonate into
- (a) Pure Sodium Carbonate represented by the formula Na<sub>2</sub>CO<sub>3</sub> and containing 43·4% of sodium. This is met with as a more or less granular white powder, feeling harsh to the touch, and easily distinguished for that reason from sodium bicarbonate which is always floury and smooth.
- (b.)—Purified Soda Ash, called in the trade Carbonate of Soda, which is also anhydrous, and contains impurities varying in amount from 40 to 60 per cent. or more, and therefore corresponding to only from 26 to 17 per cent. of sodium.
- (c.)—Washing Soda, Soda Crystals, or Crystallised Sodium Carbonate, corresponding to the formula Na<sub>2</sub>CO<sub>3</sub>+10H<sub>2</sub>O, which if pure would correspond to 16 per cent. of sodium; but the impurities constantly present bring this down to 10 per cent., or even less. The same substance is sometimes called Sal Soda, and Granulated Soda is the trade term for the crystals broken up into small pieces. In pharmacy this is simply called sodium carbonate.
- (d.)—Crystal Carbonate of Soda, which is practically pure monohydrated sodium carbonate, corresponding to the formula Na<sub>2</sub>CO<sub>3</sub> + H<sub>2</sub>O, equivalent to 37 per cent of sodium. This is met with in minute crystals, not in broken up masses like the preceding. It is called in pharmacy exseccated sodium carbonate.
- S.—Decahydrated sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>+10H<sub>2</sub>O) dissolves in about half its weight of boiling and twice its weight of cold water, the action in the latter case being accompanied by a *fall* in temperature.

Monohydrated sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>+H<sub>2</sub>O) dissolves in about one and a half times its weight of boiling water, and less than three times its weight of cold water, the solution being attended in the latter case by a *slight rise* in temperature.

Anhydrous sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) requires twice its weight of boiling water and four times its weight of cold water to dissolve it, the solution in the latter case being attended by a considerable rise in temperature.

D.—See Tests for Sodium Salts and for Carbonates. Sodium bicarbonate occasionally substituted by mistake for the carbonate may be distinguished from the latter by its floury feel (vide supra), and by the fact that a cold solution of it does not precipitate magnesium sulphate, whilst a cold solution of sodium

carbonate gives an immediate white precipitate. Another test consists in adding to a solution of each a little mercuric chloride solution, when the carbonate will give a red precipitate and the bicarbonate a white one. It must not be forgotten that the solutions must be made up with cold water, as boiling converts bicarbonate into monocarbonate.

P.—The solution acidified with nitric acid should give no precipitate with either silver or barium nitrate, denoting absence of chlorides and sulphates. The original substance should give a pure white precipitate with lead nitrate or acetate; if the precipitate is brown or black, sodium sulphide is present. A decoction of logwood mixed with the unacidified solution should not be bleached when this is treated with a quantity of sulphuric acid, almost, but not quite sufficient to neutralise it. If bleaching occurs, sodium sulphite or thiosulphate are present. To identify the latter add nitrate silver nitrate and boil, when if the white precipitate blackens, sodium thiosulphate is present.

Iron is detected with potassium sulphocyanate; calcium with ammonium oxalate, after neutralisation with hydrochloric acid; and magnesium with sodium phosphate in the filtrate from the calcium oxalate precipitate. Traces of cyanides and of arsenic are also sometimes present.

U.—Employed to render pyro, quinol, etc., alkaline, in which connection the following table, due to Mr. Walter A. Watts, may prove useful:—

 Varieties.
 Equivalents.
 Proportional Numbers.

 Anhydrous carbonate
 ...
 106
 ...
 1:000
 ·855
 ·371

 Monohydrated carbonate
 ...
 124
 ...
 1:170
 1 000
 ·434

 Decahydrated carbonate
 ...
 286
 ...
 2:698
 2:307
 1:000

# Sodium Citrate.

Syn., Citrate of Soda.

Three compounds of sodium and citric acid exist, viz.:—

Normal citrate,  $C_6H_5O_7K_3 + H_2O$ , which crystallises in deliquescent, glassy needles.

Monacid citrate, C<sub>6</sub>H<sub>6</sub>O<sub>7</sub>K<sub>2</sub>, occurring in monoclinic crystals.

Diacid citrate,  $C_6H_7O_7K + 2H_2O$ , crystallising in permanent prisms.

Of these the first is employed in photography as a restrainer, etc., and is made by completely neutralising a sclution of citric acid with sodium carbonate, and evaporating the residue to dryness at 100° C.

# Sodium Hydroxide.—NaOH.

Syn., Sodium Hydrate, Caustic Soda.

Prepared like the corresponding potassium compound (q.v.), and having similar uses.

# Sodium Nitrate. - NaNO3.

Syn., Nitrate of Soda.

Occurs native as Peruvian, Chilian, or cubical saltpetre, large quantities of which are imported for the purpose of making nitric acid (q.v.) and potassium nitrate (q.v.)

- L.—For photographic purposes the crude salt should be recrystallised several times, or the substance itself may be prepared directly by neutralising nitric acid with sodium carbonate.
  - A.—Occurs in deliquescent cubical crystals.
  - S.—Freely soluble in water.
  - D.—See Tests for Sodium Salts and for Nitrates.
- P.—The solution should give no precipitate with barium or silver nitrates, denoting absence of sulphates and chlorides.
- U.—Employed as an addition to the silver nitrate bath for sensitising albuminised paper, its use tending to keep the image on the surface of the paper. Barium Nitrate (q.v.) is also used for a similar purpose.

# Sodium Oxalate.—Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.

Syn., Oxalate of Soda.

- C.L.—Made by neutralising oxalic acid with sodium carbonate, and evaporating to dryness.
  - A.—Occurs in fine glistening needles.
- S.—Soluble in twice its weight of boiling and thirty-six times its weight of cold water.
  - D.—See Tests for Sodium Salts and for Oxalates.
  - U.—Employed in the printing-out platinotype process.

# Sodium Pyroborate.—Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>.

Syn., Sodium Biborate, Borate or Biborate of Soda, Borax.

C.—Occurs native, and is also manufactured from boro-natrocalcite (sodio-calcium-pyroborate CaB<sub>4</sub>O<sub>7</sub>·Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·18H<sub>2</sub>O), from boracite (magnesium pyroborate MgB<sub>4</sub>O<sub>7</sub>), and from orthoboric acid (H<sub>2</sub>BO<sub>3</sub>), all of which also occur naturally.

Native borax, locally known as tincal, is met with in Ladok and Great Thibet in Asia. Having been submitted on the spot to a rude refining process, it finds its way into Hindostan, whence, after being generally further purified, it is exported as refined Indian borax. To obtain pure borax from this substance it is dissolved in water, treated with slaked lime to remove fatty matters always present, next with bleaching lime to decompose the lime soap formed, after which the solution is concentrated by evaporation.

A deposit of native borax a'so occurs in Nevada, in America, on the edges of a dried-up lake, the centre of which consists of common salt. Boro-natro-calcite is found in California, and in the Salinas of Peru, Bolivia, and Chili. To convert it into borax, it is either finely powdered and boiled with a solution of sodium carbonate, when calcium carbonate is precipitated, or it is fused on the bed of a reverberatory furnace with a mixture of dry sodium carbonate and sand, when a similar change occurs. Boracite occurs at Stassfurt in Germany, and in many other localities. It is converted into boric acid by treatment with hydrochloric acid, and this into borax by the action of sodium carbonate, magnesium carbonate being precipitated.

In the lagoons of Tuscany, jets of steam mixed with boric acid issue from fissures in the ground. The natural heat is used to concentrate the dilute solutions, and the crystals of boric acid so obtained are exported as such. To convert this substance into borax, it is commonly fused with sodium carbonate, and the mass so obtained boiled with water, when the salt dissolves, and can be obtained pure by crystallisation.

A.—Occurs either in transparent crystals, more or less effloresced at the edges, or as an amorphous white powder. The crystals contain five or ten molecules of water of crystallisation, according to the temperature at which crystallisation has taken place. Those containing five molecules are octahedral, and those containing ten molecules prismatic. Borax in powder may contain from 10 to 50 per cent. of water.

- S .- Soluble in two parts of boiling and 13 parts of cold water.
- D.—When strongly heated borax intumesces or swells up to a cauliflower-like mass, which, on the temperature being still further raised, fuses to a clear glass. Solutions of borax give the reactions of a borate (q.v.)
  - U.—Employed in toning (vide Gold).

#### Sodium Silicate.

Syn., Silicate of Soda, Water Glass.

A mixture in indefinite proportions of sodium silicate (Na<sub>4</sub>SiO<sub>4</sub>) and sodium carbonate.

- C.L.—Made by fusing 15 parts of fine sand with eight parts of sodium carbonate and one part of charcoal powder.
  - A.—Occurs in white, soft lumps.
  - S.—Feebly soluble in cold, readily soluble in boiling water.
- D.—The solution mixed with an excess of hydrochloric acid, evaporated to dryness, and ignited, leaves an unsoluble white residue of silica, which remains behind when the common salt, also resulting from the reaction, has been dissolved out with water.
- U.—Employed, mixed with albumen, as a substratum for glass plates to be collodionised, etc.

# Sodium Sulphite.—Na<sub>2</sub>SO<sub>3</sub>+7H<sub>2</sub>O.

Syn., Sulphite of Soda.

- C.—Prepared by passing sulphur dioxide over damp crystals of sodium carbonate, when the following change occurs:  $Na_2CO_3 + SO_2 = Na_2SO_3 + CO_2$ .
- L.—On a small scale the process may be carried out by dissolving sodium carbonate in water, dividing the solution into two equal parts, passing well-washed sulphur dioxide through one-half until effervescence compl-tely ceases, and then mixing it with the other. The reaction in this case takes place in two stages, sodium bisulphite being first formed thus,  $\mathrm{Na_2CO_3} + \mathrm{H_2O} + 2\mathrm{SO_2} = 2\mathrm{Na\,HSO_3} + \mathrm{CO_2}$ , and this is converted into normal sulphite by the additional sodium carbonate,  $2\mathrm{Na\,HSO_3} + \mathrm{Na_2CO_3} = 2\mathrm{Na_2SO_3} + \mathrm{H_2O} + \mathrm{CO_2}$ .
- A.—Occurs in prismatic crystals, which effloresce, losing water of crystallisation, and, oxidise readily, become converted into sodium sulphate.
- S.—Soluble in four times its weight of cold and half its weight of hot water.
  - D.—See Tests for Sodium Salts and for Sulphites.
- P.—The crystals should not smell of sulphur dioxide, denoting absence of sodium bisulphite. Dissolved in cold, strong hydrochloric, free from chlorine, a solution should be obtained which gives only a slight precipitate with barium nitrate. If the precipitate is considerable it denotes the presence of large quantities of sodium sulphate in the original. The aqueous solution should be feebly alkaline. If decidedly so, sodium carbonate is probably present, and is detected by the effervesence produced when the crushed salt is mixed with a saturated cold solution of citric acid.
- U.—Employed as a so-called pyro (q.v.) preservative, and also in mercurial intensification (vide Mercuric Chloride). It has also been recommended as a fixing agent for silver prints, silver chloride, and albuminate being both soluble, with decomposition in it. Like every other readily oxidisable substance, sodium sulphite is much less stable in solution than when solid.

# Sodium Sulphantimoniate.—NaSbS<sub>3</sub>.

Syn., Sulphantimoniate of Soda, Schlippe's Salt.

- C.L.—Prepared by boiling 7oz. each of black antimony sulphide and dry sodium carbonate, 5oz of freshly slaked lime, and 2oz. of finely powdered stick sulphur, for about half an hour with 40 ounces of water. When the reaction is complete, the solution is filtered, evaporated down to small bulk, and set aside to crystallise.
  - A.—Occurs in transparent, very deliquescent crystals.
  - S .- Freely soluble in water.
- U.—Employed by some operators in intensifying collodion negatives.

# Sodium Tetraiodofluorescein.

C<sub>6</sub>H<sub>4</sub>(COC<sub>6</sub>HI<sub>2</sub>ONa)<sub>2</sub>O (vide Eosin and Fluoresceïn).

C.—Prepared by gradually adding four parts of benzol to 15 parts of Nordhausen sulphuric acid and heating the mixture first to dryness, and finally to 275°C., when meta-benzene-sulphonic acid will remain behind as a deliquescent mass. This is dissolved in water, the solution mixed with slaked lime, and the precipitate filtered off, the solution mixed with sodium carbonate, again filtered, and the residue fused with three times its weight of caustic soda. The fused mass is then dissolved in water, and the liquid boiled with hydrochloric acid until sulphur dioxide ceases to be given off. On shaking up the liquid with ether this dissolves out the resorcin formed, and which on distillation is left behind.

The resorcin is next heated to  $200^{\circ}$ C. for about thirty hours with two-thirds of its weight of phthalic anhydride (q.v.), and the crude fluorescein so obtained purified by dissolving it in caustic soda, and reprecipitating it with an excess of hydrochloric acid.

The fluoresceïn is next dissolved in caustic soda mixed with four times its weight of iodine, also dissolved in caustic soda, and the mixed solutions boiled until colourless.

An excess of acetic acid is then added to the liquid, which, having been again boiled, is mixed with caustic soda, and then strongly acidulated with hydrochloric acid, when tetraiodofluorescein is precipitated. This is finally suspended in a small quantity of boiling water, and a strong solution of caustic soda added to it in sufficient quantity to make the liquid nearly alkaline, when, on permitting the whole to cool, sodium tetraiodofluorescein will separate out.

- L.—To purify the commercial product it is dissolved in water, and the solution treated with a slight excess of nitric acid, when tetraiodofluorescein will be precipitated, which, after washing with water, can be used as such dissolved in alcohol or converted into its sodium compound by means of caustic soda.
- A.—Occurs as a brownish red powder, giving, with distilled water, a bluish red solution.
  - S.—Freely soluble in water; less soluble in alcohol.
- D.—The alcoholic solution fluoresces green, and is changed to yellow by sulphuric acid. The aqueous solution is precipitated by hydrochloric or nitric acids, and liberates vapours of iodine on being heated with manganese peroxide and sulphuric acid.
- U.—Employed in photography to render silver bromide more sensitive to yellow or orange. For this purpose the emulsion is mixed with it, or the finished plates are dipped in its solution. It is stated on good authority that the best samples of sodium tetraiodofluorescein for this purpose are those which, when converted into tetraiodofluorescein itself and dissolved in alcohol, then give a precipitate with an alcoholic solution of silver nitrate.

## Sodium Tungstate.— $Na_2WO_4 + 2H_2O$ .

Syn., Tungstate of Soda.

C.L.—Made by fusing wolfram, a mineral consisting essentially ferric and manganic tungstates with sodium carbonate. It is also obtained as a bye-product in the smelting of certain varieties of tin stone in which it is present in considerable quantity.

- A.—Occurs in tabular, nearly transparent, crystals.
- S.—Freely soluble in water.
- D.—Strong hydrochloric acid added to a boiling solution of sodium tungstate gives a yellow precipitate. Solutions of soluble tungstates left in contact with zinc and an excess of hydrochloric acid gradually yield a blue precipitate.
  - U.—Employed in toning.

# Sodium Thiosulphate.— $Na_2S_2O_3 + 5H_2O$ .

Syn., Hyposulphite of Soda, Hypo.

C.—Made commercially from tank waste or the residue of calcium sulphide (CaS) left as a bye-product in the manufacture of sodium carbonate (q v.) Two methods are adopted to convert this into hypo. (1.) The tank waste in small lumps is exposed to air for several months under cover when it becomes oxidised to calcium thiosulphate and calcium hydrate thus, 2CaS + 2O2 + H2O = CaS<sub>2</sub>O<sub>3</sub> + Ca(OH)<sub>2</sub>. On treating the mass with water the thiosulphate dissolves out, and on adding a solution of sodium sulphate to it, calcium sulphate is formed and is precipitated, sodium thiosulphate remaining in solution  $CaS_2O_3 + Na_2CO_3 = CaCO_3 +$ Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. (2.) In another process a solution of the tank waste is caused to trickle down an upright tower filled with coke, up which sulphur dioxide gas and air are passing, when it becomes converted into calcium thiosulphate thus,  $CaS + SO_2 + O = CaS_2O_3$ , which is then treated as in the first process. (3.) Sodium thiosulphate is also prepared by heating a mixture of sodium sulphate and coal dust. in a reverberatory furnace, when sodium sulphide is got thus, Na<sub>2</sub>SO<sub>4</sub> = 4C = Na<sub>2</sub>S + 4CO and this is converted into thiosulphate, by passing a current of sulphur dioxide and air through it, when the following change occurs,  $Na_2S + SO_2 + O = Na_2S_2O_3$ or if the sulphur dioxide is used unmixed with air, 2Na<sub>2</sub>S + 3SO<sub>2</sub> =  $2Na_2S_2O_3 + S$ . (4.) A fourth process consists in mixing dry sodium carbonate with sulphur and fusing the whole, when sodium sulphide is formed, and this on being boiled with water and sulphur and exposed for some time to air, becomes converted into sodium thiosulphate. The final result may be represented by Na<sub>2</sub>S + S + O<sub>3</sub> = Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. (5.) A fifth process consists in boiling caustic soda lye with sulphur until saturated, and passing sulphur dioxide gas through the liquid, the final change being analogous to that in the third process.

L.—On a small scale sodium thiosulphate may be made by passing sulphur dioxide gas through a solution of sodium carbonate until effervescence ceases, and then boiling the solution with an excess of finely powdered stick sulphur (flour of sulphur does not answer so well). The change is in this case represented by  $2NaHSO_3 + S = Na_2S_2O_3 + SO_2 + H_2O$ . It can also be made by boiling sodium sulphite with sulphur.

A.—Occurs in irregularly crystalline more or less transparent masses, which should not effloresce if pure.

S.—Extremely soluble in water. The solution does not keep very well, but if sufficient sodium carbonate be added to render it alkaline, the mixture may be kept for a considerable time. Salicylic acid has also been recommended for the purpose of preserving it. It is noteworthy that solutions of thiosulphate keep much better in the dark, than when exposed to light.

D.—A concentrated solution gives with an excess of sulphuric acid a whitish precipitate of sulphur, and with an excess of silver nitrate a white precipitate which darkens on boiling. Traces of thiosulphate may be detected by adding to the suspected liquid a drop of a solution of potassium permanganate, the pink colour of which will be destroyed. A solution of mercuric chloride which becomes mikky with even a trace of thiosulphate may also be used as a test or a dilute mixture of starch and iodine the blue colour of which it at once removes.

Another extremely delicate test for a thiosulphate is carried out by placing the substance suspected to contain it in a test tube with some pure zinc and dilute (1 to 3) hydrochloric acid. Under these circumstances the thiosulphate will become reduced to sulphide which in contact with the acid will yield sulphuretted hydrogen. This latter is readily recognised by placing a piece of white blotting paper moistened with lead acetate over the mouth of the tube which will become blackened if the merest trace of a thiosulphate is present. Heat should not be applied to the mixture, and a blank experiment should be first made with the zinc and acid, as either of these may, on account of impurities, liberate gases which will blacken the lead acetate, even in the absence of a thiosulphate.

P.—Sodium thiosulphate is very liable to contain sodium sulphate, detected by mixing an aqueous solution of it with an excess of hydrochloric acid free from chlorine, filtering off the precipitated sulphur and adding barium nitrate to the filtrate, when a white precipitate will occur if sodium sulphate was present. Samples of thiosulphate containing much sulphate effloresce or become converted into a white powder, particularly at the edges, when exposed to air.

U.—Sodium thiosulphate is used in photography as a fixing agent, its use depending on the fact that it dissolves the silver haloids (vide silver bromide). Iddine, sodium hypochlorite, hydrogen peroxide and other substances have been proposed from time to time to get rid of the excess of sodium thiosulphate left in the

fixed film. Iodine in contact with sodium thiosulphate yields sodium tetrathionate and sodium iodide thus,  $2\mathrm{Na}_2\mathrm{S}_2\mathrm{O}_3 + \mathrm{I}_2 = \mathrm{Na}_2\mathrm{S}_4\mathrm{O}_6 + 2\mathrm{NaI}$ . Sodium hypochlorite converts it into sodium bisulphate and sodium iodide,  $2\mathrm{Na}_2\mathrm{C}_2\mathrm{O}_2 + \mathrm{Na}_2\mathrm{S}_2\mathrm{O}_3 + \mathrm{H}_2\mathrm{O} = 2\mathrm{NaHSO}_4 + 4\mathrm{NaCl}$ , and hydrogen peroxide brings about a similar change thus,  $\mathrm{Na}_2\mathrm{S}_2\mathrm{O}_3 + 4\mathrm{H}_2\mathrm{O}_2 = 2\mathrm{NaHSO}_4 + 3\mathrm{H}_2\mathrm{O}$ .

Substances which act in this way are called "hypo eliminators." That they get rid of the excess of hypo is unquestionable, but as in so doing they yield products of decomposition less soluble than the hypo itself, it is difficult to see what advantage accrues from their employment.

### Sodium Salts, Tests for.

Solid salts moistened with hydrochloric acid and heated on platinum wire in the Bunsen flame colour it an intense yellow. Solutions containing sodium give with potassium antimoniate a white precipitate.

# $Starch. - (C_6H_{10}O_5)n.$

Syn., Amylose, Amylum.

C.L. - A constituent of all plants, occurring in greatest quantity in their seeds and tubers.

Flour, which is made from ground wheat, consists essentially of gluten (vide gelatin) and starch. To extract the latter the flour may be tied up in a muslin bag and kneaded beneath the surface of a considerable quantity of water, when the starch will pass through leaving the gluten behind, and on permitting the milky liquid to stand for some time the starch will be precipitated at the bottom of the vessel as a fine white powder.

In England starch is generally made from Rice, which contains about 80 % of it. The rice is first soaked for some hours in water containing 3 % of caustic soda, then thoroughly washed, finely ground, and again soaked in the alkaline ley for a couple of days. The process depends upon the fact that gluten is soluble and starch insoluble in dilute alkalies, so that the solution on being decanted off carries the gluten with it, leaving the starch behind. The pasty mass is next mixed with a large quantity of water and permitted to stand for a short time, when the heavier woody and fibrous matters sink to the bottom. The milky liquid is then decanted into another vessel, at the bottom of which it slowly deposits the starch. This is then well washed and dried at a gentle heat, when it splits up into roughly prismatic fragments, retaining about 20 % of water. Some commercial varieties are, in addition, coloured blue by a trace of ultramarine.

Starch is prepared in a similar way from potators; from Indian corn, when it constitutes corn flour; from the root of the Maranta arundinacea, when it is called arrowroot; from a species of palm, when it is known as sago; and from the roots of the Tatropha manihot, when it forms tapioca.

Chemically speaking, starch consists of granulose, inclosed in an outer cell of farmose; and of the varieties mentioned above, corn flour, being specially prepared for dietetic use, is presumably the purest and best.

S—Since the cell walls of farinose are impervious to cold water, this does not dissolve starch unless they are broken up by grinding it with sand, or some other hard body; but in hot water the inclosed granulose expands, bursts the cell walls, and dissolves, the fragments of farinose remaining, however, suspended in the liquid to which they give a characteristic opalescent appearance.

D.—The most delicate test for starch is its reaction with free iodine, which element colours it blue. To carry out the test, a weak solution of iodine is added to the liquid suspected to contain starch, both solutions being quite cold, as the colour is destroyed by heat. The presence of an excess of free chlorine, of sulphurous, or thiosulphurous acids, or of salts of the two latter, prevent the reaction from taking place.

U.—Starch is employed for mounting purposes, and for sizing certain papers. These latter are recognised by stained blue when immersed in a dilute solution of iodine.

Starch, coloured blue by iodine, is used as a test for sodium thiosulphate (vide hypo), and a stable and permanent solution for this purpose is made up as follows:—Shake up 24 grs. starch with ½ oz. water, and add to the liquid 36 grs. caustic potash dissolved in 5 oz. water. Heat the whole to boiling, and mix with it 10 grs. potassium iodide, followed by ½ oz. bromine water. A few drops of this added to a drachm of water will give a blue solution, instantly decolourised by a trace of hypo.

# Stannous Chloride.—SnCl<sub>2</sub>.

Syn., Protochloride of Tin.

C.L.—Made by boiling an excess of tin with strong hydrochloric acid, diluted with an equal volume of water,  $2HCl + Sn = SnCl_2 + H_2$ . The liquid so obtained is preserved in contact with metallic tin in a well-stoppered bottle.

U.—Employed with chlorine water as a test for gold (q.v.), with which it forms the so-called purple of cassius.

### Strontium Bromide.-SrBr.

Syn., Bromide of Strontium, Bromide of Strontia.

C. L.- Made by neutralising hydrobromic acid with strontium hydroxide (q v.), when the following change occurs 2HBr + Sr  $(OH)_2 SrBr_2 + 2\theta_2O$ .

A.—Crystallises in small tablets.

S.—Soluble in its own weight of cold water, sparingly soluble in alcohol.

D.—See Tests for Salts of Strontium and for Bromide.

U .- Employed in collo-emulsions.

# Strontium Chloride. $-\operatorname{SnCl}_2 + 6\operatorname{H}_2\operatorname{O}$ .

Syn., Chloride of Strontium, Chloride of Strontia.

C.L.—Prepared like the corresponding bromide (q.v.).

A.—Crystalkses in deliquescent prisms.

S.—Soluble in twice its weight of water, feebby soluble in alcohol.

D.—See Tests for Strontium Salts and for Chlorides.

U.-Employed in making emulsions of silver chloride in gelatine.

# Strontium Hydroxide -Sn(OH)2.

Syn., Strontium Hydrate, Hydrate of Strontia.

- C.—Made on a large scale for use in sugar refining by strongly heating an intimate mixture of strontium sulphate (occurring naturally as the mineral celestine), brown iron ore (ferric hydroxide), and coal dust, when the following change occurs:  $2SrSO_4+Fe_2(OH)_6+9C=2SrO+2FeS+9CO+3H_2O$  On treating the mass with water the ferrous sulphide remains undissolved, and the strontium oxide takes up water, becoming strontium hydroxide and passing into solution.
- L.—On a small scale the process may be carried out by making an intimate mixture of two parts finely-powdered celestine, one part of perfectly dry jeweller's rouge (ferric oxide), and one part of finely-powdered coal dust, and heating the mixture to intense redness for a couple of hours in a clay crucible. On boiling the fused mass with a large quantity of water, and filtering, syrontium hydroxide will be obtained in solution, and can be got dry by evaporating down the liquid.
  - A.—A white amorphous powder.
- S.—Sparingly soluble in water; soluble, with decomposition, in acids.
  - D.—See Tests for, Strontium Salts.
  - U.—The source of strontium bromide, etc.

### Strontium Iodide.—SrI2.

Syn., Iodide of Strontium, Iodide of Strontia.

C.L.—Prepared like the corresponding bromide (q.v.)

A.—Crystallises in yellowish-brown needles.

S.—Freely soluble in water and in alcohol.

D.—See Tests for Strontium Salts and for Iodides.

U.—Used occasionally to iodise collodion.

# Strontium Salts, Tests for.

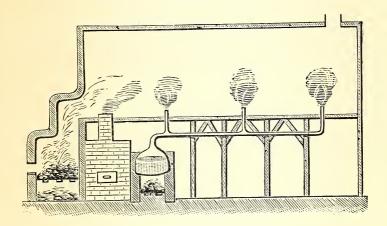
Solid salts moistened with hydrochloric acid, and heated on platinum wire in the colourless gas flame, colour it bright crimson. Solutions containing strontium give the following reactions:—(1.)

Ammonium carbonate preceded by ammonium chloride and hydroxide gives a white precipitate. (2.) Calcium sulphate gives a slowly-forming white precipitate.

# Sulphuric Acid.—H2SO4.

Syn., Hydric Sulphate, Oil of Vitriol.

C.—Made on a large scale by burning iron pyrftes (iron disulphide), and leading the sulphur dioxide so produced into a large leaden chamber into which air, steam and nitric acid vapours are also passing. The arrangement adopted is roughly sketched in the accompanying diagram, the pyrites furnace being to the left,



and the steam boiler to the right, the small furnace between the two serving to supply fumes of nitric acid, it being itself charged with a mixture of sodium nitrate and sulphuric acid. The following reactions occur during the process:—

- (a) The pyrites burn yielding sulphur dioxide, and leaving a residue of ferric oxide, thus,  $2\text{FeS}_2 + 110 = \text{Fe}_2\text{O}_3 + 4\text{SO}_2$ , this latter and air passing into the leaden chamber.
- (b) The sodium nitrate and sulphuric acid react, yielding nitric acid and disodium sulphate,  $2NaNO_3 + H_2SO_4 = 2HNO_3 + Na_2SO_4$ .
- (c) The sulphur dioxide and steam react forming sulphurous acid thus,  $SO_2 + H_2O = H_2SO_3$ .
- (d) The sulphur dioxide and nitric acid react forming sulphuric acid and nitrogen peroxide— $SO_2+2HNO_3=H_2SO_4+2NO_2$ .

- (e) The nitrogen peroxide produced (d) water, and a fresh quantity of sulphur dioxide, react to form sulphuric acid and nitric oxide— $NO_2+H_2O+SO_2=H_2SO_4+NO$ .
- (f) The nitric oxide produced in (e) and the oxygen of the air react to produce nitrogen peroxide,  $NO + O = NO_2$ .

Finally the nitric oxide produced in (f) reacts as in (e) upon a fresh supply of sulphur dioxide, and the two equations (e) and (f) repeat themselves so long as the supply of air and sulphur dioxide is kept up.

The dilute sulphuric acid so formed collects at the bottom of the leaden chamber from which it is pumped to the top of a high tower filled with coke, and through which the warm furnace gases escape, by which means most of the water it contains is got rid of. The acid strengthened in this way flows back into the chamber at the bottom of which an acid gradually increasing in strength collects, and is drawn off when it reaches a specific gravity of about 16, corresponding to 70 % of sulphuric acid. The acid so made constitutes what is known technically as chamber acid.

To further concentrate the chamber acid it is heated in open leaden pans until it reaches a specific gravity of 1.72, when it is called brown acid. To convert this into oil of vutriol it is boiled in glass or, more usually, platinum vessels, until dense white fumes begin to escape. In this condition the acid has a specific gravity of 1.84, and contains nearly 98 % of sulphuric acid. All these varieties of sulphuric acid contain lead, organic matters, and a variety of other impurities.

Pure Sulphuric Acid is made by distilling oil of vitriol, when the impurities remain behind and a colourless liquid is obtained.

Funing or Nordhausen sulphuric acid is made by passing sulphuric acid vapour over red-hot bricks, when it decomposes into water and sulphur trioxide, thus,  $\rm H_2SO_4 = \rm H_2O + SO_3$ , the latter being led into sulphuric acid, in which it dissolves, yielding the fuming acid, a mixture in variable proportions of sulphuric acid and sulphur trioxide.

A.—A heavy, oily liquid, usually coloured grey from the presence of traces of organic matter. It boils at 338°C, and its vapour forms dense white clouds when allowed to escape into air. It corrodes the skin, wood, linen, etc., by removing from these the elements of water, for which it possesses a great affinity. For this latter reason it evolves a considerable amount of heat on being diluted, rendering some care necessary when mixing the acid with water.

Like nitric and hydrochloric acids, the spec. gravity of a sample of sulphuric acid furnishes a convenient means of determining its

strength, provided, of course, other matters are absent. The following table is commonly employed for that purpose:

Spec. Gravity at 15°C.	Percentage of Sulphuric Acid.	Spec. Gravity at 15°C.	Percentage of Sulphuric Acid.	Spec Gravity at 15°C.	Percentage of Sulphuric Acid.
1'006 1'007 1'014 1'022 1'029 1'037 1'045 1'052 1'060 1'067 1'075 1'083 1'091 1'100 1'108 1'116 1'125 1'134 1'142 1'152 1'162 1'171 1'180	9 1'9 2'8 3'8 4'8 5 8 6'8 7'8 8'8 9'8 10'8 11'9 13'0 14'1 15 2 16'2 17'3 18'5 19'6 20'8 22'2 23'3 24'5	1'190 1'200 1'210 1'220 1'231 1'241 1'252 1'263 1'274 1'285 1'297 1'308 1'330 1'332 1'345 1'357 1'370 1'383 1'397 1'410 1'4'4 1'438 1'453	25.8 27.1 28.4 29.6 31.0 32.0 33.4 34.7 36.6 37.4 38.8 40.2 41.6 43.0 41.4 45.5 46.9 48.3 49.8 51.2 52.8 54.0 55.4	1.468 1.483 1.498 1.514 1.530 1.540 1.563 1.580 1.597 1.615 1.652 1.671 1.691 1.711 1.722 1.753 1.774 1.796 1.819 1.842	56.9 58.3 59.6 61.0 62.5 64.0 65.5 67.0 68.6 70.0 71.6 73.2 74.7 76.4 78.1 79.9 81.7 84.7 84.7 85.5 89.7 100.0

D.—The diluted acid gives the reactions of sulphates (q.v.)

P.—If, on evaporation to complete dryness, a residue remains it denotes lead, potassium or sodium. On dissolving this residue in a little water, these metals will pass into solution, and lead can be identified by sulphuretted hydrogen, sodium by the flame coloration, and potassium with tartaric acid.

Sulphuric acid containing lead will become milky on dilution

with water.

U.—Employed in photography in the manufacture of pyroxilin (a use dependent upon its affinity for water) and for a variety of other purposes.

Sulphates, Tests for,

Soluble salts give the following reactions: (1.) With barium nitrate or barium chloride, a white precipitate. (2.) With lead nitrate or lead acetate, a white precipitate. (3.) With a strong solution of strontium chloride, a white precipitate.

# Sulphuretted Hydrogen.—H<sub>2</sub>S.

Sun., Hydric Sulphide.

C.L.—Preparation described in part I.

A.—An inflammable gas, having a disgusting smell.

S.—Soluble to a slight extent in water, more soluble in ammonia, potash, or soda.

U.—Employed to precipitate silver sulphide from hypo., fixing

baths containing alum, also used as a valuable re-agent.

#### Sulphides, Tests for.

Solid sulphides, heated in air liberate sulphur dioxide, recognisable by its smell of burning sulphur. Most sulphides are decomposed by sulphuric acid liberating sulphuretted hydrogen (q,v)

Soluble sulphides give the following reactions: (1.) With silver nitrate or lead nitrate, a black precipitate. (2.) With sodium nitroprusside, a purple coloration.

Sulphurous Acid —H<sub>2</sub>SO<sub>3</sub>.

Syn., Hydric Sulphite.

C.—Prepared burning pyrites (vide sulphuric acid), or by heating sulphuric acid with copper, mercury, carbon, or sulphur, and leading the gas into water. The action of sulphuric acid upon copper or mercury is represented by—

 $\begin{array}{c} \operatorname{Cu} \\ \operatorname{Hg} \end{array} \left\{ \begin{array}{c} + 2\operatorname{H}_2 \operatorname{SO}_4 = \begin{array}{c} \operatorname{Cu} \\ \operatorname{Hg} \end{array} \right\} \operatorname{SO}_4 + 2\operatorname{H}_2 \operatorname{O} + \operatorname{SO}_2.$ 

With carbon its action is  $C + 2H_2SO_4 = 2H_2O = 2SO_2 + CO_2$ , and with sulphur  $S + 2H_2SO_4 = 3SO_2 + 2H_2O$ . Sulphur dioxide and water yield sulphurous acid, thus:  $SO_2 + H_2O + H_2SO_3$ .

L.—On a small scale the process is carried out as follows:—Mix four ounces of strong sulphuric acid with two ounces of water, and pour the mixture into a 20 ounce flask containing an ounce of wood charcoal broken up into small pieces. The flask is then connected to a wash bottle containing a little water, the delivery tube from which dips beneath the surface of another bottle containing 40 ounces of ice cold water. On gently heating the flask, sulphur dioxide is liberated, and is condensed in the ice cold water. At the expiration of about an hour the operation will be complete.

Îce-cold water is necessary, as at 0°C water dissolves about 20% of its weight of the gas, less than 10% being dissolved at 20°C.

A.—A colourless liquid smelling of burning sulphur, and affording by its spec. grav. a rough clue to its strength, the following tables having been compiled for that purpose:—

Spec. grav. at 15°C.	Percentage of Sulphurous Acid.	Spec. grav. at 15°C.	Percentage of Sulphurous Acid.	Spec. grav. at 15°C.	Percentage of Sulphurous Acid.
1.005	.95	1.020	4 77	1.036	8.59
1.009	1.90	1.023	5.72	1 046	9 54
1.013	2.86	1.027	6.68		
1.016	3.82	1.031	7.63		

D.—Gives the reactions of sulphites (q.v.)

P.—Mixed with an excess of hydrochloric acid, free from chlorine, it should give no precipitate with barium nitrate, denoting absence

of sulphuric acid.

U.—Employed as a pyro preservative, and as an addition to hypo baths to enable them to fix and clear at one operation. It must not be forgotten that sulphurous acid keeps badly, becoming in a comparatively short time completely oxidised.

# Sulphites, Tests for.

Solid sulphites, treated with hydrochloric acid, liberate sulphur dioxide, recognisable by its smell, and by the fact that it turns paper, moistened with potassium chromate, green.

Soluble sulphites give the following reactions: (1.) With barium nitrate a white precipitate soluble in hydrochloric acid. (2) With silver nitrate a white precipitate soluble in dilute nitric acid.

# Sulphocyanates, Tests for.

Solid salts heated with strong sulphuric acid, evolved carbon dioxide, hydrocyanic acid, and sulphuretted hydrogen. Solutions give the following reactions:—(1.) With ferric chloride a blood-red coloration. (2.) With silver nitrate a white precipitate.

#### Tartaric Acid.—C<sub>4</sub>H<sub>6</sub>O<sub>6</sub>.

C.—Obtained on a large scale from the argol or tartar deposited during the fermentation of grape juice. This contains from 70 to 90% of potassium bitartrate (KHC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>\, and is imported from Bordeaux, Marseilles, and several Italian ports. To convert it into tartaric acid it is dissolved in water, and whiting added until effervescence ceases, the solution being maintained at a temperature of 100°C. By this means calcium tartrate is precipitated, and potassium tartrate remains in solution. The latter is decanted and mixed with finely-powdered gypsum (calcium sulphate), when calcium tartrate is formed, potassium sulphate remaining in solution. Both crops of calcium tartrate are next thoroughly washed, mixed with sulphuric acid, and the liquid, after the subsidence of the calcium sulphate, is concentrated in a vacuum, the crystals redissolved in water, the solution decolorised with animal charcoal and recrystallised.

A.—Occurs as a fine white powder, or in prismatic crystals. Both varieties are quite permanent in air.

S.—Very soluble in water, fairly soluble in alcohol.

D.—(1.) The solid chars on heating with concentrated sulphuric acid. (2.) The solution neutralised with caustic soda gives, with calcium chloride, a white precipitate insoluble in boiling calcium chloride (vide citric acid). (3.) The following test will at once distinguish between citric and tartaric acids. Make the solution strongly acid with nitric acid, add an excess of silver nitrate, and filter if necessary. To the filtrate add very dilute ammonia, until the precipitate first formed is nearly but not quite redissolved. Filter again and boil, when a mirror of metallic silver will be deposited at the bottom of the tube if tartaric acid is present.

P.—Usually contains potassium and calcium salts, and trace of iron, lead, and copper. If perfectly pure, it leaves no residue when ignited, and the amount of residue, which varies from '05 to 4%, left on ignition forms a rough guide to the amount of adulteration present. If pure, tartaric acid does not deliquesce on exposure

to air. If deliquescence does occur, it is a sure sign that sulphuric acid is present, readily detectable by means of barium nitrate added to a solution rendered strongly acid by nitric acid.

U.—Employed as a preservative for sensitised paper, etc., and

in certain printing-out emulsions.

#### Tartrates, Tests for.

Solid salts blacken when heated alone, evolving the odour of burnt sugar. Heated with strong sulphuric acid, they liberate carbon monoxide and carbon dioxide. Solutions of neutral tarrates give the following reactions:—(1.) With calcium chloride, a white precipitate. (2.) With silver nitrate, a white precipitate. (3.) With potassium acetate, a white crystalline precipitate.

# Tragacanth.

Syn., Gum Dragon.

The gummy exudation yielded by the Astragalus verus and A. gummifer, and imported from Syria, Asia Minor and Persia.

- A.—Occurs as "leaf" and "vermicelli," the former being in flat strips, the latter in vermiform pieces.
- S.—As it contains only ten per cent. of true gum it is but slightly soluble in water, but swells up and becomes converted into a mucilage.
- U—Employed for mounting prints, and is said to possess weight for weight much greater adhesiveness than either gum arabic or dextrin.

# Trimethylamine.— $(CH_3)_3N$ .

- C.—Obtained on a large scale by subjecting the vinasses or residues left in the manufacture of beet sugar to destructive distillation (vide Potassium Carbonate). It can also be obtained by distilling herring brine with lime (vide Ante).
- I.—To prepare the substance on a small scale, strong alcohol saturated with ammonia gas is heated for some hours to 100°C. in a hermetically-closed vessel with methyl iodide, when a series of rather complicated reactions occur, resulting in the separation in the crystalline form of the hydriodides of mono-di and tri-methylamine. These are warmed with caustic soda, and the vapours passed through an ice-cold receiver in which the greater part of the di and tri-methylamine condense, the mono-methylamine escaping as gas. The condensed liquid is next distilled with ethyloxalate, when the dimethylamine becomes converted into a nonvolatile compound, and the trimethylamine escapes, and can be condensed in an ice-cold receiver.
- A.—An extremely volatile liquid, boiling at 10°C., and having a characteristic smell of herring brine, which contains, indeed, small quantities of it.
  - S .- Miscible in all proportions with water and alcohol.
  - U.—Employed mixed with pyrogallol in alkaline development.

# Turpentine.-Vide Rosin.

The oleo resins obtained from various species of trees, chiefly from those belonging to the pine tribs. Six varieties of it occur in commerce.

- (1) Aleppo turpentine, coming from Provence, in France, and obtained from the Aleppo pine (Pinus hatapenis).
- (2) Canadian turpentine (Canada balsam), obtained from the Balm of Gilead fir (Pinus abies), and the Balsam fir (Pinus balsamea). This is a honey-like transparent, straw-coloured body, which thickens on keeping, and is soluble in ether, chloroform, and benzol. It contains about 24 % of essential oil and 76 % of rosin, thus differing from the other turpentines, which are practically free from resin. The chief supplies of it come from the United States, Nova Scotia, and Canada.
- (3.) Chian or Cyprian turpentine, obtained from the *Pistachia terebenthinus*. The commercial supply is at present derived chiefly from the island of Chios, in the Mediterranean.
- (4.) American or Bordeaux turpentine, obtained in Russia from the Scotch fir (*Pinus sylvestris*), in Austria from the Corsican pine (*Pinus larichio*), in France from the sea fir (*Pinus maritima*), and in America from the swamp pine (*Pinus Australis*) and the red pine (*Pinus resinosa*).
- (5.) Strasburg turpentine, imported from the Vosges district of France, and obtained from the silver fir (Abies pectinata).
- (6)—Venice turpentine, coming from the Tyrol, and got from the larch (*Larix Europæa*).

All these are originally exudations from the purposely wounded tree, and are, with the exception of Canada balsam, subjected to distillation, when resin remains behind and turpentine distils over.

Most of the turpentine met with in commerce is derived from the fourth variety, even the substance sold as Venice turpentine being usually a mixture of resin and turpentine.

Crude turpentine is called simply turpentine, or oil of turpentine, and when purified by redistillation spirit of turpentine. A small quantity of the oleo-resin is imported in its natural state to make printer's ink.

- A.—Pure turpentine is a mobile white liquid, corresponding to the approximate formula  $C_{10}H_{16}$ , and having a characteristic smell. It boils at about 160° C., and has an average spec. grav. of :864.
- U.—Employed as a solvent for various resins, the solution constituting a retouching varnish.

#### Uranium.-U.

C.—Occurs naturally in pitch-blende, uranoso-uranic oxide, as uranium phosphate in uranite, as carbonate in liebigite, and in samarskite as urano-tantalite mixed with niobium and tantalum.

The first named mineral, met with in Cornwall and elsewhere, is the chief source of the metal and its salts, and contains from 40 % to 90 % of uranoso-uranic oxide (U<sub>3</sub>O<sub>8</sub>). This mineral is converted into pure uranic oxide (UO<sub>3</sub>) as follows: Having been reduced to a very fine powder it is digested with sulphuric acid, small quantities of nitric acid being added from time to time, and as soon as the powder becomes nearly white, the whole is evaporated to dryness, and the residue boiled with water Through this solution sulphuretted hydrogen is passed to precipitate most of the other metals, and the filtrate from the precipitate is oxidised with nitric acid and mixed with an excess of ammonia. The precipitate so obtained is well washed, and digested with a concentrated solution of ammonium carbonate. containing free ammonia when it dissolves, forming the double carbonate of uranium and ammonium, which is crystallised out by evaporating down the solution. On igniting this, ammonia and carbon dioxide escape, and pure uranic oxide remains, from which the uranium salts can be prepared (vide ante).

Uranium forms uranous, uranic and uranyl salts. Uranous salts are derived from uranous oxide  $\mathrm{UO}_2$ , uranic salts from uranic oxide  $\mathrm{UO}_3$ , and these latter admit of the replacement of a portion of their acidulous radical by oxygen yielding oxy salts or uranyl salts. Thus uranic chloride is  $\mathrm{UCl}_6$ , uranyl chloride being  $\mathrm{UO}_2\mathrm{Cl}_2$ . Similarly uranic nitrate is  $\mathrm{U(NO}_3)_6$ , the oxy nitrate or uranyl nitrate being  $\mathrm{UO}_2(\mathrm{NO}_3)_2$ . Only the uranyl salts are of photographic importance.

# Uranyl Chloride.—UO2Cl2.

Syn., Uranium Oxychloride.

C.L.—Made by dissolving uranic oxide in hydrochloric acid, thus,  ${\rm UO_3} + 2{\rm HCl} = {\rm UO_2Cl_2} + {\rm H_2O}$ .

A.—Occurs in flat, deliquescent, greenish-yellow plates.

S.-Freely soluble in water and in alcohol.

D.—See Tests for Uranium Salts and for Chlorides.

U.—Used in small quantities to tone silver prints. For this purpose it is employed in strongly alkaline solution, and probably acts by replacing silver by metallic uranium. Under the influence of light, uranyl chloride becomes converted into a mixture of uranous chloride and uranous oxide, and can on that account be employed as a sensitive coating for paper For instance, paper coated with a mixture of this salt and of potassium chloroplanite will, after exposure to light and treatment with hot potassium oxalate, develop a platinum uranium image.

# Uranyl Nitrate. $-\text{UO}_2(\text{NO}_3)_2 + 6\text{H}_2\text{O}$ .

Syn., Uranium Oxy-nitrate, Nitrate of Uranium.

C.L.—Made by dissolving uranic oxide in nitric acid, thus,  $UO_3 + 2HNO_3 = UO_2(NO_3)_2 + H_2O$ .

- A .- Crystallises in yellow-lemon fluorescent prisms.
- S.—Soluble in half its weight of water; fairly soluble in alcohol.
- D.—See Tests for Uranium Salts, and for Nitrates.
- U.—It becomes converted by light into a mixture of uranous nitrate and oxide, and as the former will reduce silver, gold, and platinum solutions, an image in any of these metals may be obtained by floating paper coated with uranyl nitrate and exposed to light on alkaline solutions of silver, gold, and platinum.

Mixed with silver nitrate and dissolved in collodion it can be employed to print out an image, as the uranous nitrate formed by the action of light will, at the moment of its formation, attack and reduce the silver nitrate.

Mixed with potassium ferricyanide it yields a brown solution, containing uranyl ferricyanide and potassium nitrate, thus,  $K_6Fe_2Cy_{12} + 3UO_2(NO_3)_2 = (UO_2)_3Fe_2Cy_{12} + 6KNO_3$ , and if this solution be poured over a negative intensification results, owing to the metallic silver of the latter becoming converted into silver ferrocyanide, uranyl ferrocyanide being simultaneously formed, thus,  $2_1UO_2)_3Fe_2Cy_{12} + 2Ag_2 = Ag_4FeCy_6 + 3(UO_2)_2$  FeCy<sub>6</sub>. Since the brown uranyl ferrocyanide is not completely insoluble in water, negatives so intensified must not be washed for too long a time, otherwise the uranyl ferrocyanide will be washed away, and the intensification will consequently disappear.

#### Uranium Salts, Tests for.

Solutions of these give the following reactions:—(1.) With ammonium sulphide, a slowly subsiding brownish-yellow precipitate, which forms only in neutral solutions. (2) With ammonia, a yellow precipitate. (3.) With ammonium carbonate, a yellow precipitate, readily soluble in exce-s. (4) With potassium ferrocyanide, a brownish red precipitate.

#### Wax.

Syn., Beeswax.

C.L.—Yellow Wax is the honeycomb of the bee, purified by melting it in hot water, allowing the impurities to subside, and casting the wax in suitable moulds. It occurs in tough, compact yellowish or brownish masses, smelling of honey.

White Wax is made by exposing thin cakes of yellow wax to light and air, when they become bleached. It may also be made by treating yellow wax with chromic acid, thus: Melt the wax and shake it up with a hot 10 % solution of potassium dichromate, strongly acidulated with sulphuric acid, and wash out the excess of bichromate by agitating the wax with boiling water. The faint greenish colour usually left by this treatment may be removed by a boiling solution of oxalic acid.

White wax is rather more brittle than yellow wax, and possesses a higher melting point.

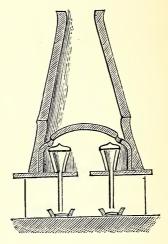
S.—Soluble in turpentine, benzol, ether, &c.

P.—If the wax feels greasy to the touch, suct is probably present. Resin is detected by shaking up the melted wax with strong alcohol, and evaporating this to dryness, when a residue of resin will remain. Vegetable and earthy matters are detected by the residue left behind on dissolving the wax in turpentine or benzol. Foreign fats are readily detected by determining the melting point of the wax, which should never exceed 66° C.

U.—A solution of wax in benzole or turpentine is employed as an encaustic paste for giving a glossy surface to silver prints.

#### Zinc.-Zn.

C.—Occurs in nature chiefly as blende or zinc sulphide (ZnS), and calamine or zinc carbonate (ZnCO<sub>3</sub>). To obtain metallic zinc, the ore is first roasted, either alone, or, if it contains any tungsten (vide Sodium Tungstate), with sodium carbonate. By this treatment the sulphide, or carbonate, is converted into oxide (ZnO), which is then mixed with charcoal, and heated in large crucibles, placed in a furnace similar to that shown in the diagram,



when the following decomposition occurs, ZnO + C = Zn + CO, and the metallic zinc, being volatile, distils off and collects in the receptacle placed underneath the furnace, and connected with a hole made in the bottom of each crucible.

If the zinc ore contains cadmium (q.v.), this will be found in the first portions of the distillate.

A.—A bluish-white metal. Granulated zinc is made by melting it (conveniently in an iron ladle) and pouring the molten mass.

from a height into water. Zinc dust is the metallic zinc condensed as fine powder in the flues of the furnace during the smelting of zinc ores.

S.—Soluble in sulphuric acid, liberating hydrogen, which will reduce moist silver chloride, hydrochloric acid being simultaneously formed.

Hydrochloric acid also dissolves zinc, and the hydrogen liberated will combine with the sulphur of a thiosulphate to form sulphuretted hydrogen (vide Sodium Triosulphate). Hydrochloric acid is most suitable for this purpose, as sulphuric acid will, under certain circumstances, itself become partially reduced to sulphuretted hydrogen when placed in contact with metallic zinc Compounds of zinc are occasionally present in cadmium salts.

# Zinc Salts, Tests for.

Soluble salts give the following reactions:—(1.) With ammonium sulphide, a dirty white precipitate. (2.) With ammonium hydrate, a white precipitate, soluble in excess. (3.) With potassium ferrocyanide, a yellowish-white precipitate. (4.) With potassium ferricyanide, an orange precipitate.

# PART III.

#### PHOTOGRAPHIC FORMULARY.

In this part I give a series of formulæ employed in photography, classified alphabetically and numbered consecutively. The numbers in brackets given after most of these refer to connected operations. Thus, each emulsion formulæ is referred to suitable developers, and these latter back again to the corresponding emulsion.

#### Clearing Solutions.

Any substance which is a feeble solvent of metallic silver acts as such. Of course, the solution must be rather dilute, otherwise a certain amount of reduction will occur. With a silver haloid in collodion a solution of potassium cyanide is effective, when the silver haloid is mixed with gelatine other agents work better.

#### Clearing Solutions for Collodion:-

- 1. Potassium cyanide, 30 grs.; water, 1 oz.
- 2. Ferric chloride, 10 grs.; water, 1 oz.
- 3. Potassium cyanide, 60 grs.; iodine, 5 grs.; water, 16 ozs.

#### Clearing Solution for Gelatine:-

- 4. Saturated solution of alum, 20 ozs.; hydrochloric acid, 1 oz.
- 5. Alum, 2 ozs.; citric acid, 1 oz.; water, 10 ozs.
- 6. Ferric chloride, 50 grs.; potass. bromide, 30 grs.; water, 4 czs.
- 7. Alum, 1 oz.; citric acid, 1 oz.; ferrous sulphate, 3 ozs.; water, 20 ozs.
  - 8 Potassium iodide, 1 oz.; water, 2 ozs.
  - 9. Chloralum solution, 1 oz; water, 2 ozs.
- 10. Chrome alum, 120 grs.; sulphuric acid, ½ drachm; water, 20 ozs.

# Collodion.

A solution of pyroxiline in ether-alcohol, ranging in strength from 1 to 20 %, according to circumstances, and either plain or iodised the iodides, and bromides used with the latter being, of course, limited to such as are soluble in ether-alcohol. Castor oil is added to enamel and transfer collodion for the purpose of toughening the film.

Plain Collogion for Iodising:-

11. Alcohol-ether, 10 oz.; pyroxilin, 60 grs.

#### Enamel Collodion:-

- 12. Alcohol (82), 48 oz.; ether (72), 84 oz.; pyroxilin, 1 oz.; castor oil, 10 minims.
- 13. Ether, 10 oz.; alcohol, 10 oz.; pyroxilin, 120 grs.; castor oil, 10 drops.

#### Transfer Collodion:-

- 14. Ether (·73), 5 oz.; alcohol (·805), 10 oz.; castor oil, ½ oz.; pyroxilin, ½ oz.

  Ferrotype Collodion (36 to 39):—
- 15. Ammonium iodide, 35 grs.; cadmium iodide, 25 grs.; cadmium bromide, 25 grs.; pyroxilin, 60 grs.; ether-alcohol, 10 oz.
- 16. Cadmium iodide, 50 grs; am nonium bromide, 20 grs; proxilin, 100 grs.; ether (72), 10 oz.; alcohol (.805, 10 oz.

#### Collodion for Collo-Enlargements (41):-

- 17. Ammonium iodide, 4 grs.; plain collodion (No. 11), 1 oz.
- 18. Cadmium iodide, 5 grs.; plain collodion (No. 11), 1 oz.

#### Collodion for Negatives (42-44):-

- 19. Cadmium iodide,  $4\frac{1}{2}$  grs.; cadmium bromide, 2 grs.; plain collodion (No. 11), 1 oz.
- 20. Ammonium iodide, 4 grs.; cadmium bromide, 14 grs.; plain collodion (No. 11), 1 oz.
- 21. Cadmiumiodide, 2½ grs.; ammonium iodide, 1½ grs.; cadmium bromide, 2 grs.; plain collodion (No. 11), 1 oz.
- 22. Ammonium iodide, 3 grs; cadmium iodide, ½ gr.; ammonium bromide, 13 grs.; plain collodion (No. 11), 1 oz.

# Collodion for Photo-mechanical Work (45):—

23. Pyroxilin, 260 grs.; ether alcohol, 42 oz; alcohol, 4½ oz.; calcium chloride, 25 grs.; cadmuim bromide, 120 grs; ammonium iodide, 72 grs.

# Collodion for Glass Positives (37 to 40):—

24. Cadmium iodide, 50 grs; ammonium bromide, 20 grs.; pyroxilin, 100 grs.; ether (·72), 10 oz; alcohol (.805), 10 oz.

# Collodion for Transparencies (46-47):—

- 25. Alcohol, 1 oz,; sodium lactate, 4 minims; sodium iodide, 8 grs.; sodium bromide, 2 grs; sodium chloride, 2 grs.; ether, 1 oz.; pyroxilin, 12 grs.
- 26 Ammonium iodide, 4 grs.; cadmium bromide, 2 grs.; pyroxilin, 4 grs.; ether-alcohol, 1 oz.

# Detergent.—A Mixture for Cleaning Glass.

For Removing Old Films from Gelatin Negatives:-

27. A saturated solution of washing soda.

For Removing Old Collodion Films:-

28. Nitric acid, 1 oz.; water 6 oz.

For Cleaning Opals:-

29. A 2 % solution of caustic soda.

For Cleaning Plain Glass:-

30. Alcohol, 100 oz.; tripoli, 5 oz.; iodine, 1 oz.

31. Water, 5 oz; alcohol, 5 oz; potass. iodide, 15 grs.: iodine, 3 grs. Mix, and add sufficient tripoli or prepared chalk.

32. Potassium bichromate,  $\frac{1}{2}$  oz.; water, 2 oz.; sulphuric acid, 1 drachm.

#### Developer.

The name used to denote any substance capable of producing a visible image from the nucleus of silver reduction product, etc. formed by the action of light.

#### Developers may be classified into-

A.—Feeble reducing agents, which decompose free silver nitrate, either present on the wet film or added to the developer, the reduced silver being then deposited as such on the portions of the negative upon which light has acted. The following developers belong to this class:—

Developer for Albumin Transparencies (190-191-203).

33. (a) Pyro, 2 grs.; citric acid, 3 grs.; water, 1 oz.

(b) Silver nitrate, 20 grs : citric acid, 60 grs.; water, 1 oz.

A few drops of (b) to the requisite quantity of (a).

Developer for Prints on Plain Paper (188-201) :-

34. (a) Saturated solution of gallic acid, 1 part; water, 4 parts.

(b) Silver nitrate, 10 grs.; water, 1 oz.

A few drops of (b) to the requisite quantity of (a).

35. (a) Pyrogallol, 2 grs; citric acid, 1 gr.; water, 1 oz.

(b) Silver nitrate, 10 grs.; water, 1 oz.

A few drops of (b) to the requisite quantity of (a).

#### Developer for Ferrotypes (15-16): -

36. Ferrous sulphate, 1 oz.; acetic acid, 1 oz.; water, 16 oz.; alcohol quant. suff., with a few drops of silver nitrate solution.

Developer for Glass Positives or Ferrotypes (15-16-24):-

37. (a) Barium nitrate, 130 grs.; water, 2 oz.

(b) Ferrous sulphate, 140 grs.; water, 2 oz.

Mix, filter, and add nitric acid 20 minims, and alcohol quant. suff., with silver nitrate at time of using.

- 38. Ferrous sulphate, 20 grs.; glacial acetic acid, 20 minims; alum, 40 g·s.; water, 1 oz.; with silver nitrate at time of using.
  - 39. (a) Saturated solution of ferrous sulphate, 1 oz.
    - (b) Tannin, 5 grs.; water, 1 oz.; nitric acid, 5 minims.

Mix, filter, and make up to 12 oz.; add silver nitrate as required.

#### Developer for Glass Positives (24).

40. Ferrous sulphate. 150 grs.; potassium nitrate, 100 grs.; glacial acetic acid, ½ oz; water, 10 oz.; nitric acid, 5 minims; alcohol, ½ oz.; with silver nitrate at time of using.

#### Developer for Collo-Enlargements (17-18).

41. Pyro, 100 grs.; citric acid, 60 grs.; glacial acetic acid, 2 oz.; water, 20 oz.; with silver nitrate at time of using.

#### Developer for Collodion Negatives (19-22).

- 42. Pyro, 1 gr.; glacial acetic acid, 20 minims; water, 1 oz.; alcohol quant. suff., with silver nitrate at time of using.
- 43. Ferrous sulphate, 10 to 60 grs.; glacial acetic acid, 10 to 20 minims; water, 1 oz; alcohol quant. suff., with silver nitrate at time of using.
- 44. Ammonio-ferrous sulphate, 25 grs.: glacial acetic acid, 25 minims; water, 1 oz.; alcohol quant. suff., with silver nitrate when using.

# Developer for Photo-Mechanical Work (23):—

45. Water, 35 ozs.; sulphuric acid, 20 drops; ferrous sulphate, 620 grs.; alcohol, 1 oz. with silver nitrate when using.

#### Developer for Dry Collodion Transparencies (25-26):—

- 46. Ferrous sulphate, 5 grs.; glacial acetic acid, 5 minims; water, 1 oz.; alcohol, quant. suff., with silver nitrate when using.
- 47. Citric acid, 2 grs.; pyro, 2 grs.; water, 1 oz, with silver nitrate when using.
- B.—Powerful reducing agents, which decompose the reduction product formed by exposing the silver haloids to light.

Developer for Negatives on Silver Bromide, Bromo-Iodide, or Bromo-Chloro-Iodide in Gelatin (116 to 120):—

- 48. (a) Ferrous sulphate, 160 grs.; water, 1 oz.
  - (b) Potassium oxalate, 1 oz.; water, 3 ozs.

Take four parts (b) to one part (a).

49. Borax, 100 grs; potass oxalate, 400 grs; ferrous salphate, 120 grs; water, 6 ozs. Boil, filter, and dilute with four parts water.

- 50 Sodium phosphate, 50 grs; ammonium oxalate, 200 grs; ferrous sulphate, 75 grs. Dissolve by boiling with 4 ozs. water. Filter, and dilute with four parts wat r
- 51. Potassium oxalate, 440 grs; sodium sulphite 60 grs; water, 6 ozs. Dissolve, and add ferrous sulphate 160 grs, and filter.
- 52. Neutral ammonium tartrate, 200 grs.; borax, 50 grs; water, 3 ozs; ferrous sulphate, 50 grs. Boil and filter.
  - 53. (a) Saturated solution potassium oxalate with \$\frac{9}{10}\$th % of ammonium bromide.
    - (b) Saturated solution ferrous sulphate with 2 ths % of tartaric acid. Take four parts (a) and one part (b).
  - 54. (a) Hydroquinone, 5 grs; water, 5 ozs.
    - (b) Ammonia, 60 minims; water, 9 drachms

For every 4 ozs. of (a) use from 10 to 30 minims of (b).

- 55. (a) Hydroquinone, 10 grs; water, 10 ozs
  - (b) Potassium carbonate, a saturated solution.

For every ounce of (a) use 10 to 60 minims (b).

- 56. Hydroquinone, 1 gr.; sodium carbonate, 2 grs.; sodium sulphite, 2 grs.; potass. bromide, ½ gr.; water, 1 oz.
- 57. Hydroquinone, 100 grs.; sodium sulphite, 400 grs.; potassium carbonate, 300 grs.; water, 20 oz.
  - 58 (a) Hydroquinone, 80 grs.; citric acid, 10 grs.; sodium sulphite, 80 grs.; water, 20 oz.
    - (b) Caustic potash, 160 grs.; sodium sulphite, 160 grs.; water, 20 oz.
    - (c) Potass. bromide, 24 grs.; water, 1 oz.

Use equal parts (a) and (b) and (c) up to 10 minims.

- 59. (a) Hydroquinone, 4 grs.; potass. metabisulphite, 4 grs.; potassium bromide, 1 gr.; water, 1 oz.
  - (b) Caustic potash, 10 grs.; water, 1 oz.

Equal parts (a) and (b).

- 60. (a) Hydroquinone, 160 grs.; sodium sulphite, 2 oz.; citric acid, 60 grs.; potassium bromide, 20 grs.; water up to 20 oz.
  - (b) Potassium carbonate, 2 oz.; crystallised sodium carbonate, 2 oz.; water up to 20 oz.

Equal parts of (a) and (b).

- 61. Cream of tartar, 90 grs.; potassium sulphite, 45 grs.; potassium carbonate, 4 oz.; water, 16 oz. Boil, filter, and add hydroquinone ½ oz. For use mix one part with sixteen of water.
  - 62. (a) Hydroxylamine hydrochlorate, 32 gis.; citric acid-15 grs.; potassium bromide, 20 grs.; water, 1 oz.
    - (b) Caustic soda, 60 grs.; water, 1 oz.

Take 1 drachm (a), water  $2\frac{1}{2}$  oz., and from 10 to 60 drops (b).

- 63. (a) Hydroxylamine hydrochlorate, 2 grs.; caustic soda, 3 grs; potassium bromide, ½ gr.; water, 1 oz.
- 64. (a) Hydroxylamine hydrochlorate, 32 grs; citric acid, 15 grs; water, 1 oz.
  - (b) Potassium carbonate, 480 grs.; sodium carbonate, 480 grs.; water, 10 oz.

Take 30 minims (a), 120 minims (b), and  $1\frac{1}{2}$  oz. water.

- 65. (a) Pyrocatechin, 15 grs.; water, 7 oz.
  - (b) Potass-carbonate, 300 grs.; water, 4 oz.

Mix an ounce (a) with from one to three drachms (b).

- 66. (a) Pyrocatechin, 1 oz.; sodium sulphite, 4 oz.; water, 40 oz.
  - (b) Caustic potash, 8 oz; water, 80 oz.

One volume (a) to two volumes (b).

- 67. (a) Eikonogen, 75 grs.; sodium sulphite, 75 grs.; water, 4 oz.
  - (b) Caustic potash, 50 grs.; water 2 oz.

Two vols. (a), one vol. (b).

- 68. Eikonogen, 1 oz.; caustic potash, 1 oz.; sodium sulphite, 1 oz.; water, 100 oz.
- 69. Eikonogen, 5 grs.; potassium carbonate, 5 grs.; sodium carbonate, 15 grs.; sodium sulphite, 25 grs; water, 1 oz.
- 70. Eikonogen, 15 grs.; potassium carbonate, 30 grs.; sodium sulphite, 80 grs.; water, 1 oz.
  - 71. (a) Sodium sulphite, 6 oz.; water, 64 oz.; pyro, 1 oz.; with sufficient citric acid to acidify the mixture.
    - (b) Sodium carbonate, 3 oz.; potassium carbonate, 1 oz.; water, 64 oz.

Take equal volumes.

- 72. (a) Sodium sulphite, 4 oz.; water, 4 oz.; sulphurous acid, 4 oz.; pyro, 1 oz.
  - (b) Potassium carbonate, 3 oz.; water, 8 oz.; sodium sulphite, 2 oz.

Take one drachm (a), from 10 to 30 minims (b), and 2 ounces water, adding more of (b) as development proceeds up to 2½ drachms.

- 73. (a) Pyro, 4 grs.; sodiam bisulphite, 12 grs.; water, 1 oz.
  - (b) Crystal carbonate soda, 96 grs.; water, 1 oz.

Equal volumes.

74 - The following, compiled by Messrs. Lyonel Clark and E. Ferrero, of the Camera Club, are the

PYROGALLOL DEVELOPERS
Recommended for Various Plates by their respective Manufacturers.

The Quantities are given in Grains and Minims per Ounce of Developer.

	The Quantit	ies are given i	n Grains and	The Quantities are given in Grains and Minims per Ounce of Developer.	Unnce of De	vetoper.			
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6	3.60	:	: :	:	: :	22	:	08.81	:
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	1.20	0 63	:	3.16	:	:	:	:	:
Beechey (Dry Col.)	12	:	m	:	:	:	30	:	:
Beernaert	4.28	:	÷	:	16.05	:	:	32.10	:
Britannia	61	81	:	4	፥	:	:	:	:
Cadett's	1.20	3	:	9	:	:	:	:	:
Charterhouse	98.1	3.40	:	1.3e	:	:	:	2,72	:
Cranbourne		:	0.72	2.30	:	:	:	01.1	:
Derby		2 to 4	፥	1.60 to 4.00		:	:	:	:
Derwent		:	:	:		:	:	38.4	:
Pap. Neg.		:	:	:	61	:	:	2.7	:
S		:	:	:	19	:	:	27	:
Do. Do.	3.53	:	:	:	12	က	:	21.18	:
	8	0 50	:	8	:	:	:	:	64
Edward's XL		:	0.20	64	:	:	:	:	:
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Ditto, Instantaneous		:	:	:	፥	8 60	:	17	:
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# PYROGALLOL DEVELOPERS - (Continued).

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Sodium Sulphite.	Grains.	:	22	:	:	:	:	:	01	:	:	:	9	:	:	:	:	:	21		:	:	21.60 to 40.40	:
Ammonium Carbonate.	Grains	:	:	:	:	:	:	:	:	:	:	:	:	:	:	;	:	:	:		:	:	:	;
Potassium Carbonate.	Grains.	:	8.75	:	:	:	:	:	6.41	:	:	:	:	:	4	:	:	:	:		:	:	12 to 30	:
Sodium Carbonate.	Grains.	:	:	:	:	:	:	:	:	:	:	:	:	:	:	4	:	:	†I		:	:	:	:
.ninomm A	Minims.	4.20	:	64	и	48.1		4.20	:	2	1.87	as I is to 4	3		:			3.75	:		3	3	:	2.50 to 4
Potassium Bremide,	Grains.	:	:	0.27	:	0.23	:	:	:	0.83	0.23	Ammonia	0.75	9†.0	0.12	0.12	:	:	0.20		:	0.20	.:	
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PL.1TES.		Facilis	Froedman's Tissue	German (Dr.	Do. Kingston, Spect.	German (Sands and Hui	Globe	Ilford	Keystone	Lancaster's		Manchester, No. 1	Do. No. 2	Do. No. 3 SulpPyro	Do. No. 4 do. (Potash)	Do. No. 5 do. (Soda)		Do. New Cheap		Do. Photo-Mechanical	Lantern	:	Mayfield's Spcl. Fav.	Miall's

# PYROGALLOL DEVELOPERS-(Continued).

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Peta sium Carbonate.	Grains	: : <b>:</b> :
Sodium Carbonate.	Grains,	7.50 to 11'25
ъ:потт А	Minims. 0.60 to 4 2 to 4 2 to 4 0.83 or more 2 in: 2 in: 2 in: 2 in: 2 in: 3 in: 2 in: 3 i	25°0 25°0 2°
Potassium Bromide.	Crains	0.33
Ammonium A Bromide.	Grains. 0 20 100 40 1 50 0 22 0 0 1 more 2 90 0 45 2 50 1 726 1 726 1 1 726 1 1 726 1 1 726 1 1 726 1 1 726 1 1 726 1 1 726 1 726	: : : :
.ovva	Grains.  2 2 2 2 2 5 6 6 8 7 8 7 8 7 8 7 8 7 8 7 8 7 8 7 8 7	e m m c
PLATES.	Midland Monckhoven's Morgan and Kidd's Do. Richmond National Nelson Perenter Paget's Premier Rouch's Soho Tranagas Tranagas	nwrigl nwrigl nwrigl hutter nwrigl

#### Developers for Photo-Mechanical Work on Gelatine Plates (116 to 120).

- 75. (a) Potassium metabisulphite, 192 grs.; potassium bromide, 256 grs.; pyro, 192 grs.; water, 1 oz.
  - (b) Ammonia, 1 oz.; water, 19 ozs.
- 2 vols. (a), one vol. (b).
- 76. (a) Potassium metabisulphite, 192 grs.; potass. bromide, 48 grs.; water, 20 ozs.; pyro, 96 grs.
  - (b) A saturated solution common washing soda.
- 8 vols. (a), one vol. (b).
- 77. (a) Hydroquinone, 80 grs.; potassium metabisulphite, 120 grs; potassium bromide, 5 grs.; water, 20 ozs.

(b) Caustic potash, 200 grs.; water, 20 ozs.

Equal volumes (a) and (b).

Developers for Prints on Gelatino-bromide Paper (113, 114, 115):—

- 78. (a) Ferrous sulphate, 12 ozs.; water, 20 ozs.; sulphuric acid, 10 drops.
  - (b) Potassium oxalate, 8 ozs.; water, 20 ozs.; oxalic acid, 4 grs.
  - (c) Potassium bromide, 60 grs.; water, 1 oz.

Take 2 ozs. (a),  $2\frac{1}{2}$  drachms (b), 6 drops (c).

- 79. (a) Hydroquinone, 12 grs.; potass. metabisulphite, 8 grs; glycerine, ½ oz.; water, ½ oz.
  - (b) Caustic soda, 20 grs.; water, 1 oz.

Equal volumes.

- 80. (a) Ammonio-ferrous sulphate, 480 grs.; potassium metabisulphite, 120 grs.; water, 5 oz.
  - (b) Potassium oxalate, 4 ozs.; water, 20 ozs.; oxalic acid, 4 grs.

Take one vol. (a), 4 vols. (b).

- 81. (a) Eikonogen, 90 grs.; sodium sulphite, 450 grs.; water, 30 oz.
  - (b) Dried sodium carbonate, 1 oz; water, 1 oz.

Three vols (a), one vol (b).

Developers for Transparencies on Gelatino-bromide of Silver (109 to 112):—

- 82 (a) Hydroquinone, 80 grs.; potass. metabisulphite, 40 grs water, 20 ozs
  - (b) Potassium carbonate, 800 grs.; water, 20 ozs.

Equal volumes of (a) and (b), with 2 to 10 drops of a 10% solution of potassium bromide.

- 83. (a) Hydroquinone, 80 grs.; sodium sulphite, 1 oz. potassium bromide, 15 grs.; water, 10 oz.
  - (b) Caustic potash, 50 grs.; water, 40 oz.

Equal volumes.

- 84. (a) Potassium oxalate, 2 oz.; oxalic acid, 20 grs.; water, 7 oz.
  - (b) Ferrous sulphate, 1½ oz.; sulphuric acid, 5 drops; water, 5 oz.
  - (c) Potass bromide, 120 grs.; water, 1 oz.

6 drachms (a), 2 drachms (b), 20 minims (c).

- 85. (a) Pyro, 20 grs.; sodium sulphite, 90 grs.; citric acid, 5 grs.; water, 10 oz.
  - (b) Ammonia, 30 minims; potassium bromide, 3 grs.; water, 10 oz.

Equal volumes.

Developers for Transparencies on Gelatino-chloride of Silver (121, 122):—

- 86. (a) Ferrous sulphate, 80 grs.; sulphuric acid, 1 drop; water, 1 oz.
  - (b) Potass citrate, 200 grs.; potass, oxalate, 60 grs; water, 1 oz.

Equal volumes.

- 87. (a) Potass oxalate, 2 oz.; ammonium chloride, 40 grs.; water, 2 oz.
  - (b) Ferrous sulphate, 4 drachms; citric acid, 2 drachms; alum, 2 drachms; water, 16 oz.

Equal volumes.

- 88. (a) Potassium oxalate, 3 oz.; water, 34 oz.
  - (b) Ferrous sulphate, 6½ drachms; citric acid, 30 grs.; potass. bromide, 3 grs.; water, 18 oz.

Equal volumes.

- 89. (a) Citric acid, 1 oz.; water, 4oz. Dissolve exactly, neutralise with ammonia, and add 10 grs. citric acid and 2 grs. common salt.
  - (b) Ferrous sulphate, 120 grs.; sulphuric acid, 2 drops; water, 1 oz.

Three vols. (a) to one vol. (b).

- 90. (a) Hydroquinone, 43 grs.; sodium sulphite, 320 grs.; ammonium bromide, 2 grs.; water, 10 oz.
- (b) Ammonium carbonate, 200 grs.; water, 10 oz. Equal volumes.

91. The following formulæ have been worked out by Mr. Cowan for use with his transparency plates (Marion & Co.) according to the colour the finished transparency is to be:—

The quantities are given in grains per ounce.

_		_		_	_					
	Ferrous Sulphate.	Citric Acid.	Ammonium Carbonate.	Ammonium Citrate.	Sodium Chloride.	Magnesium Carbonate.	Sodium Carbonate.	Potassium Carbonate.	Potass. Oxalate,	Potass.Citrate
Slaty blue Greenish brown Sepia brown Clear red brown Warm grey brown Deep red brown Green blue Sepia red Sepia yellow Blue black Intense blue-black Blue	35 35 35 35 35 35 35 35 35 35 35 35	90 90 90 67 <sup>1</sup> / <sub>2</sub> 60 30 90 22 <sup>1</sup> / <sub>2</sub>	37½	? 187½ 124½	6	57 183 111 132	153 <sup>2</sup> 115 <sup>1</sup> ⁄ <sub>2</sub>	873 1003	4½2 24 24 24 33	18 9 75 102

C.—Substances which, like potassium oxalate, dissolve ferrous oxalate, and so enable it to react upon a readily-reducible metallic solution present in the paper (92, 93 and 94), or added to the potassium oxalate (95).

Developer for Hot Bath Platinotype (216):—

- 92. Potassium oxalate, 130 grs.; water, 1 oz.; heated from 76° to 83°C.
- 93 (For sepia tones). Potassium oxalate, 10 oz.; water, 40 oz.; oxalic acid, 150 grs.; copper chloride, 2 oz; filter and heat to 90°C.

94 (For brown tones). Potassium oxalate,  $9\frac{1}{2}$  oz.; water, 35 oz.; heat to boiling, and add 80 grs. mercuric chloride dissolved in  $3\frac{1}{2}$  oz. water; filter and use at 80°C.

# Developer for Cold Bath Platinotype (217):—

- 95. Potassium oxalate, 30 grs.; potassium phosphate, 30 grs.; potassium chloroplatinite, 10 grs.; water,  $1\frac{1}{2}$  ozs.
- D.—Substances which react upon the product of insolation so as to change its colour.

Developer for Pizzighelli's Cyanotype (219-223):—

96. Potassium ferricyanide, 50 grs.; water, 1 oz.

Developer for Pellet's Cyanotype (219-223):—

- 97. Potassium ferrocyanide, a saturated solution.
- E.—Substances which, like potassium sulphocyanate or warm water exert a solvent action, upon ordinary gelatine, but do not dissolve that substance when mixed with potassium dichromate and exposed to light.

Developers for Carbon Process (207):-

- 98. Potassium sulphocyanate, 50 grs.; water, 1 oz.
- 99. Water heated to 30° 40° C.

#### Emulsion.

A viscous fluid holding in suspension a sensitive silver salt. Emulsions are conveniently sub-divided into

A.—Printing out emulsions, in which an excess of silver nitrate is present, and on which the image is "printed out."

Gelatino-chloride Emulsions (237, 238, 239).

- 100. (a) Nelson's No. 2 gelatine, 240 grs.; water, 42 ozs.
  - (b) Silver nitrate, 225 grs.; water, 13 ozs.
  - (c) Potass. citrate, 63 grs.; sodium chloride, 63 grs.; water, 1½ ozs.
- Add (b) to (a), and emulsify into (c). When emulsified add 6 drachms alcohol and 1 drachm water containing 9 grains salicylic acid and 1 grain chrome alum.
  - 101. (a) Sodium chloride, 40 grs.; potass. citrate, 20 grs.; water, 1 oz.
    - (b) Silver nitrate, 120 grs.; water, 1 oz.
    - (c) Heinrich's emulsion gelatine, 320 grs.; water, 3½ ozs.
  - Mix (b) and (c), and emulsify into (a).
  - 102. (a) Silver nitrate, 6 grs.; water, 6 drachms; gelatine, 230 grs.
    - (b) Lithium chloride, 1 gr.; tartaric acid, 1 gr.; water, 1 drachm.

Emulsify (b) into (a).

- 103. (a) Lump sugar, 24 grs.; citric acid, 9 grs.; tartaric acid, 3 grs.; potassium bromide, 1½ grs.; water, 4 oz.
  - (b) Nelson's hot gelatine, 60 grs.; sodium chloride, 36 grs.;
     (a) solution, 1½ ozs.; ammonium carbonate, 12 grs.;
     liquid albumen, 24 minims; water, 6½ ozs.
  - (c) Silver nitrate, 240 grs.; water, 3½ ozs.
  - (d) Isinglass, 300 grs.

Dissolve (b) by heat, let cool somewhat, and emulsify into (c', let stand 15 minutes, pour over (d), and when swelled dissolve, and let ripen for 24 hours. Re-dissolve, and add \(\frac{1}{2}\) oz. alcohol.

#### Collodio-chloride Emulsions (242):-

- 104. (a) Alcohol, 1 oz.; ether, 1 oz.; pyroxylin, 12 grs.
  - (b) Silver nitrate, 60 grs.; water, 1 drachm.
  - (c) Strontium chloride, 64 grs.; alcohol, 2 ozs.
  - (d) Citric acid, 64 grs.; alcohol, 2 oz.

Mix 30 minims (b) with (1), add a drachm of (c), and half a drachm of (d). Shake well, and cost at once.

B.—Emulsions for development in which no free silver nitrate is present. The excess of soluble salts left by double decomposition are either removed by (a) washing the emulsion before coating, when it is said to be a washed emulsion; (b) washing the plates themselves after coating, when it is said to be an unwashed emulsion. The latter plan is practicable with collodion only.

Collodio-Bromide Washed Emulsion (Transparency) (82 to 85): -

- 105. (a) Pyroxiline, 60 grs.; ether,  $2\frac{1}{2}$  ozs.; alcohol (805),  $2\frac{1}{2}$  ozs.
  - (b) Ammonium bromide, 63 grs.; water, 60 minims; alcohol (\*805), ½ oz.
  - (c) Silver nitrate, 100 grs.; water, 60 minims; nitric acid, three drops.

Add (b) to (a), and emulsify (c) into the mixture. Set aside for 24 hours to ripen, let solvents evaporate, wash, dry, and dissolve in 8 ozs. ether-alcohol.

Collodio-Bromide Washed Orthochromatic Emulsion (82 to 85):-

- 106. (a) Ether (·72, 4 ozs.; alcohol (82), 4 ozs.; pyroxiline, 60 grs.; erythrosin, 1 gr; crystallised cadmium bromide, 120 grs.
- (b) Silver nitrate, 120 grs.; water, 1 drachm; alcohol, ½ oz; Emulsify (b) into (a). Set aside 24 hours to ripen, let solvents evaporate, wash, dry, and dissolve in 8 ozs. ether alcohol.

Collodio-Bromide Unwashed Emulsion (82 to 85):-

- 107. (a) Alcohol, 1 oz; ether,  $2\frac{1}{2}$  ozs.; pyroxiline, 37 grs.
  - (b) Zinc bromide, 200 grs.; alcohol, ½ oz.; nitric acid, 4 drops.
  - (c) Alcohol, 1oz.; ether, 2½ ozs.; pyroxiline, 37 grs.
  - (d) Silver nitrate in powder, 330 grs.; water, 2 drachms; alcohol,  $1\frac{1}{2}$  ozs.
- Add (b) to (a) and (d) to (c), and emulsify former into latter.

Make up to 15 ozs with alcohol-ether, let ripen for 24 hours, coat, and wash plates.

- 108. (a) Cadmium bromide, 16 grs.; ammonium bromide, 8 grs.; alcohol, 1 oz.; ether, 1oz.; pyroxiline, 10 grs.
  - (b) Silver nitrate, 36 grs.; water, 18 minims.

Emulsify (b) into (a), let stand 12 hours, and then add cadmium bromide, 4 grs.; ammonium bromide, 2 grs.; dissolved in a drachm of alcohol. Let ripen 24 hours, coat, and wash plates.

Gelatino-Bromide Emulsions (Transparency) (82 to 85):-

- 109. (a) Silver nitrate, 50 grs.; citric acid, 50 grs.; ammonia, 90 minims; water, 4½ ozs.; Nelson's No. 1 gelatine, 20 grs.
  - (b) Potassium bromide, 45 grs.; gelatine as above, 20 grs.; carbolic acid, 5 drops; water, 4½ ozs.

Heat both solutions to  $60^{\circ}$  C., and emulsify (a) into (b). When cool pour over 250 grs. Nelson's emulsion gelatine, and when softened melt, let set, and wash.

- 110. (a) Ammonium bromide, 60 grs.; ammonium iodide, 20 grs.; Nelson's emulsion gelatine, 180 grs.; water, 5 ozs.
  - (b) Silver nitrate, 120 grs.; nitric acid, 2 drops; water, 5 ozs.

Heat to 60° C., emulsify (a) into (b), let set, and wash.

111. (a) Ammonium bromide, 35 grs.; ammonium chloride, 30 grs.; Nelson's gelatine, 180 grs.; water, 5 ozs.

(b) Silver nitrate, 120 grs.; nitric acid, 2 drops; water, 5 ozs.

Heat to  $60^{\circ}$ C, emusify (a) into (b), let set, and wash.

112. (a) Potassium bromide, 18 grs.; potass iodide, 1 grain; Nelson's gelatine, 120 grs.; water, 2 ozs.

(b) Silver nitrate, 24 grs.; water, 2 ozs.; ammonia sufficient to just redissolve precipitate first formed.

Heat to  $40^{\circ}$  C., emulsify (a) into (b), let set, wash, re-melt, and make up to 8 ozs.

Gelatino-bromide Emulsions (for developed Prints on Paper or Opal, 78 to 81):—

113. (a) Nelson's No. I gelatine, 100 grs.; ammonium bromide, 150 grs.; ammonium iodide, 20 grs.; ammonium chloride, 50 grs.; water, 10 ozs.

Dissolve, acidify with hydrochloric acid, heat to 40° C., add 450° grs. silver nitrate in crystals, and shake well till dissolved. When cool, but not set, pour over 400 grs. Nelson's No. 2 gelatine, previously soaked in water; melt, let set, and wash.

- 114. (a) Silver nitrate, 100 grs.; citric acid, 100 grs.; water, 3 ozs.
  - (b) Sodium chloride, 17 grs.; potassium bromide, 40 grs.; citric acid, 100 grs; Nelson's No. 1 gelatine, 40 grs.; water, 3 ozs.

Emulsify (b) into (a), let cool, pour over 200 grs Nelson's emulsion gelatine, previously swelled in water; melt, let cool, and wash.

- 115. (a) Nelson's No. 1 gelatine, 42 grs.; potassium bromide, 26 grs.; water, 1 oz.
  - (b) Silver nitrate, 32 grs.; water, 1 oz.

Emulsify at 60°C, let set, and wash.

Gelatino-Bromide Emulsion (negative), Boiling Method
(48 to 74):—

116. (a) Silver nitrate, 40 grs.; water, 8 ozs.

(b) Ammonium bromide, 220 grs.; ammonium iodide, 15 grs.; ammonium chloride, 15 grs.; Ne son's No. 1 gelatine, 80 grs.; water, 8 ozs.; hydrobromic acid, sufficient to acidify.

(c) Nelson's emulsion gelatine, 450 grs. Emulsify (a) into (b), boil until blue, let cool, pour over (c), let set, and wash.

Gelatino-Bromide Emulsion (negative), Double Decomposition Method (48 to 74):—

117 (a) The equivalent in hydrobromic acid of any convenient strength of 150 grs. silver nitrate, water 7 ozs., Nelson's No. 1 gelatine 40 grs.

(b) 150 grs. silver nitrate precipitated by sodium bi-carbonate, the precipitate being well washed and suspended in a solution containing 30 grs. Nelson's No 1 gelatine

in 7 ozs. water.

Add (a) to (b), shake well, and keep at 50°C until desired sensitiveness is obtained. Let cool, pour over 150 grs. Nelson's emulsion gelatine, re-melt, and coat. This requires no washing, as the products of decomposition are carbon dioxide and water.

Gelatino-Bromide Emulsion (negative), Ammonia Method (48 to 74):—

118 (a) Silver nitrate, 200 grs.; water, 4 ozs.; perchloric acid, 5 drops.

(b) Potassium bromide, 170 grs.; potass. iodide, 10 grs.; Nelson's emulsion gelatine, 40 grs.; water, 6 ozs.

Add ammonia to (a) until solution is just clear. Heat (b) to 60°C and emulsify (a) into it. Heat until blue, let cool, pour over 200 grains dry gelatine; re-melt, let set, and wash.

Gelatino-Bromide Emulsion (negative), Precipitation Method
(48 to 74):—

119 (a) Nelson's No 1 gelatine, 30 grs.; potass. bromide, 160 grs.; potassium iodide, 10 grs.; water, 10 ozs.

Heat to 60°C, and add 200 grs. silver nitrate in crystals.

Shake until dissolved, boil till blue, add five drops ammonia, boil again for a minute or two, let stand for some time, decant liquid from silver bromide, wash this several times with water and add to it 300 grs. Nelson's No 1 gelatine dissolved in 15 oz. water.

Orthochromatic Gelatin Emulsion. Negative (48 to 74):-

120. (a) Potassium bromide, 135 grs.; %ths% alcoholic solution of erythrosin, 40 minims; Nelson's No. 1 gelatine, 20 grs.; water, 2 oz.

(b) Silver nitrate, 170 grs.; water, 2 oz.

Heat to 60°C, emulsify (b) into (a), boil till blue, let cool, pour over 200 grs. Nelson's emulsion gelatine; re-melt, let set, and wash.

Gelatino-Chloride Emulsion. Transparency (86 to 91):—

- 121. (a) Sodium chloride, 80 grs.; Nelson's No 1 gelatine, 30 grs.; Hydrochloric acid, 5 minims; water, 14 oz.
  - (b) Silver nitrate, 200 grs.; water, ½ oz.
  - (c) Nelson's No. 1 gelatine, 30 grs.; water, 1 oz.

Mix (b) and (c), heat to 60°C., and emulsify (a) into mixture. When emulsified pour over 240 grs. Nelson's emulsion gelatine swelled and dissolved in 2 oz. of water; mix well, let set, and wash.

122. (a) Silver nitrate, 950 grs.; water, 10 oz.

(b) Sodium chloride, 480 grs; Nelson's special emulsion gelatine, 480 grs.; water, 15 ozs

(c) Nelson's emulsion gelatine, 480 grs.; water, 5 oz.

Heat three solutions to  $60^{\circ}$ C., mix (a) and (c), and emulsify mixture into (b). Let set and wash.

#### Fixing Solutions.

Water containing a salt capable of dissolving with decomposition a silver haloid, whilst exerting little or no effect upon metallic silver, pyroxiline, or gelatine.

### Fixing Baths for Collodion (15 to 26):-

123. Pctass. cyanide, 25 grs.; water, 1 oz.

124. Hypo, 120 grs.; water, 1 oz.

Fixing Solutions for Gelatine Emulsions (100 to 122):—

125. Hypo, 1 oz.; sodium bisulphite, ½ oz; water, 4 ozs.

126. Hypo, 1 oz.; water, 4 ozs.

Fixing Solutions for Albuminised Paper (189 to 191): -

127. Hypo, 5 ozs.; water, 30 ozs.; ammonia, 2 drams.

128. Sodium sulphite, 2 ozs; water, 5 ozs.; acidified with sulphuric acid.

129. Water, 1 gallon; hypo, 1lb.; sod. bicarb., 1 teaspoonful; common salt, 1 teaspoonful.

#### Intensifier.

A substance which increases the visual or optical opacity of the silver image.

These may be sub-divided into

A —Density intensifiers which act by depositing metallic silver on the image, such as :—

# Collodion Intensifiers:—

130. Pyro, 2 grs.; citric acid, 2 to 4 grs.; 10 grs. solution silver nitrate, 2 to 6 drops; water, 1 oz.

131. Ferrous sulphate, 5 grs.; citric acid, 10 to 20 grs.; 10 grs. silver nitrate solution, 2 to 6 drops; water, 1 oz.

#### Gelatine Intensifier :-

- 132. (a) Gelatine,  $15\frac{1}{2}$  grs; glacial acetic acid, 200 minims; water 334 minims.
  - (b) Ferrous sulphate,  $46\frac{1}{2}$  grs; water,  $3\frac{1}{2}$  ozs.

(c) Silver nitrate, 15½ grs.; glacial acetic acid, 60 minims; water, 2 ozs.

Mix ½ oz. (b) with 40 drops (a), and soak plate in mixture. Then return to glass containing 3 to 10 drops (c). Mix well, and reapply to plate.

- 133 (a) Silver nitrate, 100 grs; water, 2 ozs.
  - (b) Ammonium sulphocyanate, 240 grs.; water 10 ozs. Mix, collect precipitate, and dissolve it in 10 ozs. of a 5 % solution of hypo.

To intensify take 1 oz of this solution, 3 grs. pyro, 12 grs. sulphite soda, 6 minims ammonia, and 2 grs. potass. bromide.

- 134. (a) Hydrokinone, 10 grs; water 2 ozs.; citric acid 6 grs.
  - (b) Silver nitrate, 16 grs; water, 1 oz.

Mix 3 vols. (a) with 1 vol (b), and apply to negative.

B.—Substitution intensifiers in which other substances wholly or partially take the place of the silver.

#### Collodion Intensifiers :-

- 135. Convert silver image into silver iodide by immersion in potass. iodide, 2 grs.; iodine, 1 gr.; water, 1 oz.; and darken with potassium permanganate, 18 grs; water, 1 oz.
- 136. Convert image into silver iodide as in 130, and blacken with uranium nitrate, 60 grs.; potassium ferrioyanide, 60 grs.
- 137. Convert image into iodide as in 130, and blacken with gold chloride, 1 gr.; water, 20 oz.
- 138. Bleach with mercuric chloride, 20 grs.; hydrochloric acid, 4 drops; water, 1 oz; and blacken with ammonium sulphide, 1 oz.; water, 30 oz.
- 139. Bleach as in 133, and blacken with ammonia, 1 drachm; water, 1 oz.
- 140. Soak in lead nitrate, 20 grs.; potassium ferricyanide, 30 grs; water, 1oz.; and blacken with ammonium sulphide, 1 oz.; water, 5 oz.

#### Gelatin Intensifiers.

- 141. Bleach with mercuric chloride saturated aqueous solution, strongly acidified with hydrochloric acid, and blacken with ammonia, 1 drachm; water, 1 oz
- 142. Bleach as in 136, and blacken with ammonia, 1 oz.; hypotoz.; water, 5 oz.
- 143. Bleach as in 136, and blacken with ammonium sulphide, 1 oz.; water, 10 oz
- 144. Bleach as in 136, and blacken with a strong ferrous oxalate developer.
  - 145. (a) Mercuric chloride, 308 grs.; potassium bromide, 308 grs.; water, 36 oz.
    - (b) Silver nitrate, 308 grs.; water, 18 oz.
    - (c) Potassium cyanide, pure, 308 grs.; water, 18 oz.
- Mix (b) and (c) in equal volumes, and add half the quantity of a). Immerse plate in mixture until blackened.

- 146. Mercuric chloride, 15 grs.; potassium iodide, 46½ grs.; water, 7 oz. Immerse until intensified.
  - 147. (a) Mercuric chloride, 60 grs.; water, 7 oz.
    - (b) Potassium iodide, 90 grs.; water, 2 oz.
    - (c) Hypo, 180 grs.; water, 2 oz.

Mix (b) and (c), wash precipitate, and dissolve it in (c). Immerse plate in mixture until intensified.

148. Uranium nitrate, 15½ grs.; potass. ferricyanide, 15½ grs.; water, 3½ oz. Immerse plate in mixture until intensified.

#### Mountants.

Substances to cause paper to adhere to card-board. These must not be acid, and must be without action upon silver. With all but indiarubber solutions the mountant is best applied to the slightly damped surface.

- 149. Arrowroot, 150 grs.; Nelson's No.1 gelatine, 150 grs.; water' 3 oz. Dissolve, and when cold add alcohol, 2 drachms; carbolic acid, 3 drops.
- 150. Starch, 1 drachm; water, 1 oz. Heat till dissolved, and add ½ drachm glycerine.
- 151. Gum arabic,  $\frac{1}{2}$  oz.; dextrin,  $1\frac{1}{2}$  oz.; water, 5 oz.; carbolic acid, 2 drops.
  - 152. Dextrin, 1 oz.; water, 3 oz.; alcohol, ½ oz.
- 153. Tragacanth, 120 grs.; alcohol, 6 drachms. Mix to a paste, transfer to 9 ozs. water and shake well.
- 154. Dextrin, 1 oz.; lump sugar, ½ oz.; alcohol, ½ oz.; boiling water, 3 oz.
- 155.—Nelson's No. 1 gelatin, 200 grs Soak in half-ounce water and dissolve by heat, add 5 ozs. alcohol with constant stirring, and boil for 15 minutes.
- 156. Nelson's No. 1 gelatin, 4 oz.; water, 16 oz.; glycerine, 1 oz. Soak, dissolve by heat, add 5 ozs. alcohol, and boil till uniform.
- 157. Best bonnet glue, 4 oz.; water, 20 oz. Soak for two hours, pour off water, melt, add 3 oz. water mixed with 8 oz. alcohol, and stir well till mixed; then add 2 oz. glycerine and 20 drops of carbolic acid.
  - 158. Bleached lac,  $\frac{1}{2}$  oz.; alcohol, 1 oz. Dissolve by heat.
  - 159. Masticated rubber, 80 grs.; benzol or chloroform, 8 oz.

# Orthochromatising Solutions

have for their object to render a gelatino bromide plate dipped in them more sensitive to the red end of the spectrum.

7. 160. Soak for two minutes in ammonia, 2 oz.; water, 200 oz.; then dip for one minute in 10th per cent. aqueous solution of eosin, 25 oz.; water, 175 oz.; ammonia, 4 oz.

Cyanin blue and quinolin red may be substituted for the eosin.

161.—Soak plate in alcoholic solution of chlorophyl for a minute wash thoroughly and dry.

162. Soak for two minutes in silver nitrate, 20 grs; ammonium carbonate, 90 grs.; water, 16 oz; ½% alcoholic solution of erythrosin, 10 drachms. After exposure and before development plunge for 30 secs. in potass bromide, 120 grs.; ammonia, ½ oz.; water, 10 oz.

#### Preservative.

A term used to denote

A.—A substance which acts as a halogen absorbent and so enables an image visible or invisible to be more readily impressed. This is properly called by exact writers a sensitiser. An example of it is afforded by the free silver nitrate present in albumenised sensitive paper or in the various

#### Dry Collodion Preservatives (25).

- 163. (a) Gum arabic, 20 grs.; sugar candy, 5 grs.; water, 6 drachms.
  - (b) Gallic acid, 3 grs.; water, 2 drachms.

Mix and filter

- 164. Boiling water,  $5\frac{1}{2}$  oz.; ground coffee,  $\frac{1}{2}$  oz.; let stand for an hour, filter, mix with a solution of gum arabic, 90 grs.; sugar candy, 120 grs.; water,  $5\frac{1}{2}$  oz.; and again filter.
  - 165. Pure tannin, 20 grs.; water, 1 oz.
- 166. Liquid albumen, 1 oz.; ammonia, 1 drachm; water, 1 oz.; shake to a froth, filter, and mix with table beer or stout, 1 oz.
- 167. Water, 7½ oz.; gum arabic, 90 grs.; sugar candy, 90 grs.; tannin, 15 grs.
- 168. A saturated solution of red gum in equal parts of alcohol and water.
- 169. Pyro, 4 grs.; gum arabic, 80 grs.; sugar, 80 grs.; water, 8 oz. (This is unsuitable for collo-bromide.)
- B.—A substance which retards the decomposition of silver albumino-chloride by atmospheric agencies (not light). As an example of this we have

Preservatives for Sensitised Albuminised Paper (189 to 191).

- 170. Float back of paper on potass. citrate, 1 oz.; water, 30 oz.
- 171. Float back of paper on water, 100 oz.; gum arabic, 3 oz.; hydrochloric acid, 2 oz.; citric acid, 2 oz.; tartaric acid, 2 oz.
  - 172. Float back of paper on water, 100 oz.; citric acid, 31 oz.
- 173. Float back of paper on water, 20 oz.; tartaric acid, 1 oz.; gum arabic half oz.

#### Reducer.

Denotes in photography

A.—Substances which remove the silver image by dissolving it per se as in

#### Collodion Reducer.

174. Potassium cyanide 80 grs., water 1 oz.

B.—Substances which convert the silver image into other compounds, either soluble in salts applied with the substance which brings about this conversion, or in salts in which the altered plate is subsequently immersed. Example of such reducers are found in the following—

#### Collodion Reducer.

175. Potassium cyanide 40 grs.; iodine 2 grs.; water 1 oz.

#### Gelatin Reducers.

- 176. Ferric chloride, 60 grs.; water, 1 oz.; soak, wash, and return to fixing bath.
- 177. Bleaching lime, 2 oz.; potassium carbonate, 4 oz.; dissolve each in water, mix, boil and filter. Soak plate in solution so obtained, wash and return to fixing bath.
- 178. Alum, 4 oz.; copper sulphate, 4 oz.; common salt, 8 oz; water, 40 oz.
  - 179. Potassium ferricyanide, 3 grs.; hypo, 30 grs; water, 4 oz.
- 180. Potassium bichromate, 10 grs.; nitric acid, 10 drops; water, 20 oz.
- 181. Ferric chloride, 90 grs; citric acid, 75 grs.; water, 4 oz. Soak, wash, and return to fixing bath.
- 182. Copper chloride, 2 grs.; water, 20 oz. Soak, wash, and return to fixing bath.

# Salting Solutions.

These are mixtures containing soluble chlorides, bromides, or iodides, etc, and applied to paper, etc., prior to sensitising it with silver nitrate. The soluble haloids decompose the silver nitrate, leaving insoluble silver haloids in the pores of the paper. The following are types of such mixtures:—

Salting Solutions for Plain Paper Prints (printed out) (204):—

- 183. Ammonium chloride, 250 grs.; Nelson's No. 1 gelatin, 15 grs.; water, 30 oz.
- 184. Ammonium chloride, 100 grs.; barium chloride, 100 grs.; sodium citrate, 20 grs.; water, 20 oz.
- 185. Ammonium chloride, 80 grs.; sodium chloride, 30 grs.; sodium citrate, 100 grs.; gelatin, 10 grs.; water, 10 oz.
  - 186. Sodium chloride, 300 grs.; water, 20 oz.

187. Ammonium chloride, 100 grs.; sodium citrate, 100 grs.; gelatin, 20 grs.; water, 10 cz.

188. Frankincense, 10 grs.; gum mastic, 8 grs.; calcium chloride, 10 grs.; water, 1 oz.

Salting Solutions for Albuminised Paper (printed out) (127 to 129):—

189. Ammonium chloride, 200 grs.; alcohol,  $\frac{1}{2}$  oz; water,  $4\frac{1}{2}$  oz; liquid albumen, 15 oz.

Salting Solution for Plain Paper Prints (developed) (34, 201):—

190. Potassium iodide, 10 grs.; potassium chloride, 40 grs.; tapioca, 20 grs.; lemon juice, 16 minims; distilled water, 1 oz. Dissolve salts in water, add lemon juice, mix tapioca with a little of the liquid, and mix it with the remainder raised to boiling point. Strain through muslin, and brush over paper.

191. Sodium chloride, 10 grs.; hydrochloric acid, 6 minims; water, 10 ozs. Float for two hours.

Albumen Transparency Salting Solutions (developed) (33 203).

192 (a) Celloidin, 2 grs; ether-alcohol, 1 oz.

Coat with this, and when set immerse in the following:-

(b) Albumen, 1 oz.; potassium iodide, 2 grs.

193 Coat with pyroxilin, as in (a), and immerse in albumen, 5 ozs; potassium iodide, 35 grs.; lump sugar, 300 grs; iodine, 1 gr.; water,  $\frac{1}{2}$  oz.

# Sensitising Solutions.

These consist of

A. Silver nitrate, as in the following:—

Collodion Sensitising Baths (Positive) (15 to 26).

194 Silver nitrate, 1 oz.; barium nitrate, 40 grs.; potassium iodide, 1 gr.; distilled water, 12 oz.; glacial acetic acid, 2 minims.

195. Silver nitrate, 5 ozs.; water, 80 ozs.; nitric acid, 10 minims. Saturate with silver iodide and filter.

Collodion Sensitising Baths (Negative) (15 to 26).

196. Silver Nitrate, 320 grs.; water, 8 oz; potass. iodide, 1 gr.

Sensitising Baths for Albuminised Paper (189 to 191).

197. Silver nitrate 40 to 60 grs. to the ounce of water.

198 The above bath, with 20 to 30 grs. of ammonium, lead, or barium nitrate to the ounce.

199. Silver nitrate, 10 ozs; sodium nitrate, 5 ozs.; loaf sugar, 2 oz; water, 120 ozs.

200. Silver nitrate, 8 ozs; ammcnium nitrate, 2 ozs.; magnesium nitrate, 1 oz; water, 64 ozs.

# Sensitising Baths for Preserved Albuminised Paper (189 to 191).

- 201. Silver nitrate 40 to 60 grs. to the ounce of water, with 20 to 30 grains of citric acid
- 202 The above bath, with 5 to 10 drops of perchloric acid to the ounce of solution.
- 203. Silver nitrate, 2 oz ; water, 20 oz.; add sodium carbonate 1 drachm and citric acid 2½ drachms.

Sensitising Bath for Plain Paper Prints (34, 189, 183).

204. Silver nitrate 40 to 60 grains to the ounce of water, with sufficient ammonia to just redissolve the precipitate first formed.

Sensitising Bath for Developed Paper Prints (190, 191, 33):—

205. Silver nitrate, 40 grs.; citric acid, 3 grs.; water, 1 oz.

Sensitising Solutions for Albumen Transparencies (Developed):— 206. Silver nitrate, 30 grs.; glacial acetic acid, 30 minims; water, 1 oz.

B.- Potassium bichromate applied to gelatine as in the following:—

Sensitising Bath for Carbon Autotype Tissue (98, 99):—

207. Potass. dichromate, 1 oz.; water, 20 oz.; ammonia, 20 minims.

Sensitising Bath for Litho Transfer Paper (99):—

- 208. Water, 35 oz; potass. dichromate, 900 grs. Add sufficient ammonia to change colour from orange to yellow. Float paper coated side uppermost for three minutes.
- C.—Potassium bichromate mixed with other substances and applied to glass, as in

# Formulæ for Dusting-on Process:

- 209. Dextrine, 60 grs; sugar candy, 80 grs.; ammonium dichromate, 30 grs.; glycerine, 2 to 8 drops; water, 30 oz.
- 210. Gum arabic, 60 grs; glucose, 45 grs.; glycerine, 10 drops; potass. dichromate, 30 grs.; water, 2 oz.
- 211. Dextrine,  $\frac{1}{2}$  oz.; glucose,  $\frac{3}{4}$  oz.; potass. dichromate,  $\frac{1}{2}$  oz.; glycerine, 2 drops; water, 10 oz.
- 212 Saturated solution of ammonium dichromate, 5 drachms; honey, 3 drachms; albumen, 3 drachms; water, 30 oz.
- 213. Honey, 4 drachms; glucose, 8 drachms; albumen, 6 drachms; dextrine, 3 drachms; potass. dichromate, 8 drachms; water, 20 oz.
  - 214. (a) Gum arabic, 1,000 grs.; loaf sugar, 1,000 grs.; mercuric chloride, 5 grs.; water, 40 oz.; alcohol, 10 oz.
    - (b) Ammonium dichromate, 2 ozs.; water, 20 ozs.

Three volumes (a) and one volume (b).

215. Sugar candy, 4 drachms; gum arabic 5 drachms; ammonia dichromate, 4 drachms; water, 10 ozs.

D.—Ferric oxalate, mixed with oxalic acid, etc., as in the following:—

Sensitising Solution for Hot Bath Platinotype (92 to 94):—

216.—Potassium chloro-platinite, 210 grs.; ferric oxalate, 260 grs.; oxalic acid, 180 grs.; water, 10 ozs

Sensitising Solution for Cold Bath Platinotype (95):—

217.—Ferric oxalate, 480 grs.; oxalic acid, 48 grs.; mercuric chloride, 2 grs.; water, 4 ozs.

Sensitising Solutions for Printing-out Platinotype:

- 218. (a) Potassium chloro-platinite, 1 oz.; water, 6 ozs.
  - (b) Sodio-ferric oxalate, 40 ozs.; powdered gum arabic, 40 ozs.; 3 % solution of sodium oxalate, 100 ozs.; glycerine, 3 ozs.

Warm sodium oxalate solution to 50°C, add glycerine, and dissolve sodio-ferric oxalate in the mixture. Pour this over gum arabic, let stand till dissolved, shake well, let settle for a day, and decant.

- (c) Potassium chlorate, 192 grs.; (b) solution, 100 oz.
- (d) 5 % solution mercuric chloride, 20 ozs.; 3 % solution sodium oxalate, 40 ozs; powdered gum arabic 24 ozs.; glycerine, 2 ozs.

For black tones take 5 vols. (a), 6 vols. (b), 2 vols. (c).

For brown tones take 5 vols. (a), 4 vols. (c), 4 vols. (d).

Sensitising Solutions for Cyanotype (96, 97):—

- 219. (a) Ferric ammonium citrate, 120 grs.; water, 1 oz.
  - (b) Potass. ferricyanide, 75 grs.; water, 1 oz.

Mix in equal volumes, and coat paper. This is developed by being merely washed in water.

- 220. (a) Gum arabic, 5 oz.; water, 25 oz.
  - (b) Ferric ammonium citrate,  $2\frac{2}{3}$  oz.; water,  $5\frac{1}{3}$  oz.
  - (c) Ferric chloride,  $1_3^2$  oz.; water,  $3_3^1$  oz.

Mix in equal volumes.

- 221. (a) Common salt, 3 oz.; ferric chloride, 8 oz.; tartaric acid, 3\frac{1}{4} oz.; water, 50 oz.
  - (b) Gum arabic, 25 oz.; water, 50 oz.

Mix in equal volumes.

- 222. Ferric chloride, 616 grs.; oxalic acid, 308 grs.; water, 14 oz.
- 223. Ferric chloride, 48 grs.; citric acid, 40 grs.; gum arabic, 42 grs.; water, 11 oz.

#### Substrata.

A thin layer of rubber, gelatine, etc., interposed between the sensitive substance and the glass for the purpose of ensuring adhesion.

#### Substrata for Collodion or Gelatine:-

- 224. Albumen, 1 oz.; water, 20 oz.
- 225. Rubber paste, 3 grs.; choloform, 1 drachm; petroleum ether, 7 drachms.
  - 226. Dried albumen, 50 grs.; water, 50 oz; ammonia, 5 drops.
  - 227. Albumen, 1 oz.; sodium silicate, 1 oz.; water, 20 oz.
  - 228. Gelatine, 75 grs.; water, 60 oz.; ammonia, 2 drachms.
- 229. Gelatine, 50 grs.; glacial acetic acid, 4 drachms; alcohol, 6 drachms; chrome alum, 10 grs.
  - 230. Rubber paste, 1 gr.; chloroform or benzole, 1 oz.
- 231. Nelson's No. 1 gelatine, 60 grs.; water, 8 oz. Dissolve, add 2 drachms of a ten grain to the oz. solution of chrome alum, shake vigorously and filter.
- 232. Albumen, 1 oz.; water, 20 oz.; alcohol, 1 oz.; carbolic acid, 10 drops.

#### Toning Solutions.

A.—Liquids containing gold, platinum, etc, usually mixed with the salt of a feeble acid, which, when brought in contact with the reduction product metallic silver, or (sometimes) with the metal, deposits gold, etc., on it.

Toning Solutions for Wet or Dry Collodion, or Photo Crayons (15 to 26).

- 233. Platinum chloride, 1 gr.; water, 10 oz.; nitric acid, 10 drops.
  - 234. Iridium chloride, 1 gr.; water, 10 oz; nitric acid, 10 drops.
- 235. Gold chloride, 1 gr.; potassium ferricyanide, 60 grs.; uranium nitrate, 60 grs.; water, 20 oz.
- 236. Gold chloride, 2 grs.; sodium acetate, 30 grs.; water, 8 oz.; ammonium sulphocyanate, 50 grs.

Toning Solutions for Gelatino-chloride Printed out Prints, Opals, etc. (100 to 103):—

- 237. (a) Water, 12 oz.; hypo, 2 oz.; alum, 120 grs.; ammonium sulphocyanate, 60 grs.; sodium chloride, \(\frac{1}{2}\) oz. Let stand a week and filter.
  - (b) Water, 3 oz.; gold chloride, 15 grs.

Mix 40 parts of an old bath with 60 parts (a) and 7 parts (b).

238. (Toning and fixing). Hypo, 7 oz.; gold chloride, 15 grs. lead nitrate, 75 grs.; water, 40 oz.

- 239. Gold chloride, 2 grs.; ammonium sulphocyanate, 20 grs.; sodium phosphate, 20 grs.; water, 4 oz.
- Toning Solutions for Gelatino-bromide Developed Prints, Opals, etc. (113, 114, 115):—
- 240. Sodium acetate, 60 grs.; bleaching lime, 4 grs.; gold chloride, 2 grs.; water, 20 ozs.
- 241. Platinic chloride, 15 grs.; hydrochloric acid, 1 oz.; water, 70 ozs.
- 242. Uranium nitrate, 4 grs.; potassium ferricyanide, 4 grs.; water, 1 oz.
- 243 (Toning and fixing). Gold chloride, 1 gr.; hypo, 1 oz.; water, 4 ozs.
- Toning Solutions for Prints on Resined Paper (Printed-out):— 244. Gold chloride, 1 gr.; water, 10 ozs.; precipitated chalk, 5 grs.; sodium acetate, 10 grs.
- Toning Solutions for Collodio-chloride Printed-out Prints, Opals, etc. (104):—
  - 245. (a) Ammonium sulphocyanate, 1½ ozs; water, 60 ozs.; hypo, 9 grs.
    - (b) Gold chloride, 22 grs.; water, 60 ozs.
- Mix in equal volumes, add an excess of chalk, and filter.
- Toning Solutions for Prints on Albuminised Paper (189 to 191):—
  - 246. Sodium acetate, 75 grs.; gold chloride, 3 grs.; water, 30 ozs.
- 247. Sodium carbonate, 45 grs.; water, 30 ozs.; gold chloride, 3 grs.
- 248. Bleaching lime, 4 grs; gold chloride, 3 grs.; water, 30 oz.; chalk, quant. suff.
- 249. Bleaching lime, 45 grs.; gold chloride, 45 grs.; chalk, 45 grs.; sodium acetate, 180 grs; water, 15 ozs.
  - 250. Borax, 100 grs.; gold chloride, 1 gr.; water, 20 oz.
  - 251. Sodium phosphate, 100 grs.; gold chloride, 1 gr.; water, 10 ozs.
- 252. Ammonium sulphocyanate, 60 grs; gold chloride, 1 gr.; water, 20 oz.
  - 253. Pot. chloroplatinite, 2 grs.; water, 1 oz.; nitric acid, 2 drops.
  - 254. Sodium tungstate, 20 grs.; gold chloride, 1 gr.; water, 8 ozs.
- 255. Gold chloride, 15 grs.; sodium acetate, 150 grs., lime water, 15 ozs.
  - 256. Calcium chloride, 4 grs.; gold chloride, 1 gr.; water, 1 oz.
- 257. Water, 32 oz.; sodium acetate, 60 grs.; sodium chloride, 60 grs.; uranium nitrate, 4 grs.; gold chloride, 4 grs.
- 258. Gold chloride, 15 grs.; sodium bicarb., 30 grs.; sodium acetate, 360 grs.; water, 15 ozs.

- 259. Gold chloride, 1 gr.; sodium bicarb., 30 grs.; water, 10 oz.
- 260. Platinic chloride, 1 gr; water, 16 ozs.; potass. carbonate, 2 grs.; formic acid, 1 drachm.
- 261. Uranium nitrate, 1 gr.; gold chloride, 1 gr.; sodium bicarb., 20 grs.; water, 1 oz.
- 262. (Fixing and toning). Sodium acetate, 120 grs.; ammonium sulphocyanate, 120 grs.; hypo,  $2\frac{1}{2}$  oz.; water, 10 oz.; dissolve by heat, let cool, and add gold chloride, 5 grs.
- 263. (Fixing and toning). Sodium tungstate, 60 grs; ammonium sulphocyanate, 100 grs.; hypo, 960 grs.; water, 8 oz.: dissolve by heat, let cool, and add gold chloride, 6 grs.
- B.—The term toning is also applied to denote the change of colour brought about by converting the silver image into silver iodide, etc., and then blackening it by placing it in various other mixtures.

Toning Solutions for Collodion Transparencies (25):—

- 264. Convert into silver iodide and blacken by immersion in ammonium sulphide, 5 drops; water, 1 oz.
- 265. Treat as above, and blacken by immersion in gold chloride, 1 gr.; potassium ferricyanide, 60 grs; uranium nitrate, 60 grs; water, 20 oz
- 266. Bleach with mercuric chloride and blacken by immersion in a 10 % solution of liver of sulphur.

#### Varnish.

The term used to denote the coating applied to paper, glass, etc

A.—When applied to paper the mixture is known as a waxing or encaustic paste, and serves both to protect the surface and glaze it as in the following —

Encaustic Pastes for Albuminised Paper (189):—

- 267. White wax, 1 oz; turpentine or benzol, 1 oz
- 268. White wax, 500 grs.; elemi, 10 grs.; benzole,  $\frac{1}{2}$  oz; oil of lavender, 1 drachm; alcohol,  $\frac{3}{4}$  oz.
- 269. White wax, 3 oz; turpentine,  $3\frac{1}{2}$  oz.; copal varnish,  $1\frac{1}{2}$  drachm; oil of lavender,  $\frac{1}{2}$  drachm.
- 270. White wax, 100 grs; dammar varnish, 40 minims; turpentine, 100 minims.
- 271. Elemi, 60 grs; mastic, 30 grs.; Canada balsam, 60 grs; sandarac, 60 grs.; essential oil of camphor, 2 oz.
- 272. White wax, 11 oz; ether, 32 oz.; plain collodion, 24 oz. 10 % alcoholic solution of shellac, 16 oz; alcohol, 8 oz.

B.—Occasionally the object is to render the whole semitransparent by immersing the (usually) negative in such mixtures as the following—

Solution for Rendering Paper Negatives Transparent:-

273. White paraffin wax, 6 oz; petroleum spirit, 2 oz.

C.—Black varnishes are employed for backing up glass positives, as in the following—

#### Backing Varnishes for Positives (24):-

- 274 Turpentine (869), 115 oz; bitumen of Judæa, 10 oz.; white wax, 4 oz.; lampblack, 2 oz
  - 275. Asphaltum, ½ oz.; Canada balsam, 1 oz.; turpentine, 1 oz.
  - 276. Asphaltum, ½ oz.; masticated rubber, 15 grs.; benzole, 1 oz.
- 277. Asphaltum, 4 oz.; masticated rubber heated to fusion, 100 grs.; benzole, 10 oz.; turpentine, 1 oz.
  - 278. Asphaltum, 4 oz.; Canada balsam, 1 oz.; chloroform, 4 oz.
- 279. Lampblack, ½ oz.; shellac, 60 grs.; turpentine, 2 oz.; alcohol, 4 oz.
- D.—Retouching varnishes are employed to give a surface upon which the pencil will bite easily.
  - 280. (a) Alcohol, 82 oz.; sandarac, 15 oz.; turpentine, 6 oz.; oil of lavender, 5 oz.
    - (b) Alcohol, 27 oz.; ether, 2½ oz; camphor, 5 oz.; water, 10 oz.

Mix, let stand for a week, and decant.

- 281. Sandarac, 1 oz.; castor oil, ½ oz.; alcohol, 7 oz.
- 282. Turpentine, 3 oz; dammar, 80 grs.
- 283. Alcohol, 36 oz.; sandarac, 5 oz.; camphor,  $\frac{1}{2}$  oz.
- 284. Castor oil, 11 oz.; Venice turpentine, ½ oz.
- 285. Mastic, 45 grs.; ether, 2 oz.; dissolve and add benzole, 6 oz.
- 286. Dammar, 10 grs.; Canada balsam, 5 grs.; turpentine, 1 oz.
- 287. Ether, 15 oz.; sandarac, 60 grs.; shellac, \(\frac{3}{4}\) oz.; mastic, 10 grs. Dissolve and add  $2\frac{1}{2}$  oz. benzole.
  - 288. Gum arabic, 80 grs.; benzole, 1 oz.
  - 289. Canada balsam, 20 grs.; turpentine, 1 oz.
- E.—Matt varnishes are used for giving a groined appearance to the back of the glass negative.

#### Matt Varnishes for Negatives: -

- 290. Sandarac, 3 oz.; mastic, 3 oz.; ether ('72), 70 oz.; benzole ('878), 20 to 40 oz., according to the optical density required.
- 291. Sandarac, 10z.; alcohol, 6 oz. Dissolve and add 1½ drachms castor oil.

#### Matt Varnishes for Transparencies :-

- 292. A solution of white wax in ether.
- 293. Gelatine, 2 oz.; water, 6 oz. Dissolve and add glycerine  $\frac{1}{2}$  oz., and new milk, 2 oz.
- F.—Anti-halation varnishes, applied before exposure to the back of plate to counteract blurring.

#### Anti-halation Varnishes: -

- 294.—Aurine, 2 grains; plain collodion, 1 oz.
- 295.—Powdered burnt sienna, 1 oz.; gum arabic, 1 oz.; glycerine, 2 drachms; water, 10 oz. Shake well before using.
- 296.—Gelatine, 50 grs; glycerine, 2 drachms; ivory black, 30 grs.; water, 1 oz.
- G.—Varnishes proper are those used over the sensitive film to protect it. They are sub-divided into hot and cold according as the plate is heated or not after they have been applied.

#### Hot Varnishes for Negatives: -

- 297.—Bleached lac, 4 oz.; alcohol, 20 oz.; camphor, ½ oz.
- 298.—Sandarac, 4 oz.; alcohol, 30 oz; oil of lavender, 3 oz.; chloroform,  $\frac{1}{2}$  oz.
- 299.—Shellac,  $1\frac{1}{4}$  oz.; mastic,  $\frac{1}{4}$  oz.; turpentine,  $\frac{1}{4}$  oz; sandarac,  $1\frac{1}{4}$  oz; Venice turpentine,  $\frac{1}{4}$  oz.; camphor, 10 grs.; alcohol, 20 oz.
- 300.—Sandarac, 90 oz.; turpentine, 36 oz; oil of lavender, 10 oz.; alcohol, 50 oz.
- 301.—Sandarac, 2 oz.; shellac, 1 oz.; castor oil,  $\frac{1}{2}$  oz.; oil of lavender,  $\frac{1}{4}$  oz; alcohol, 20 oz.
- 302.—Alcohol, 16 oz.; shellac, 2 oz.; sandarac, 2 oz.; Canada balsam, 60 grs.; oil of lavender, 1 oz.
  - 303.—Best white hard varnish, ½ pint; alcohol, 1 pint.
  - 304.—Red shellac varnish, ½ pint; alcohol, 1½ pint.
- 305.—Sandarac, 9 oz.; shellac, 2 oz. Powder very finely, cover with absolute alcohol, let stand for two days, decant liquid, and preserve it. Repeat this four times, and mix all the solutions with sufficient alcohol to make up bulk to 80 oz., and add 1 oz. castor oil.
  - 306.—Best shellac,  $1\frac{1}{4}$  oz.; alcohol, 20 oz.
- 307.—Bleached lac, 8 oz.; orange shellac, 4 oz.; sandarac, 1 oz.; alcohol, 60 oz. Shake up with broken glass until dissolved.
  - 308. Dammar, 70 grs.; resin, 6 grs.; turpentine, 4 oz.
  - 309. Shellac, 5 oz.; copaiba balsam, ½ oz.; alcohol, 50 oz.
- 310. Printer's turpentine, 16 oz.; Venice turpentine, 16 oz.; sandarac, 80 oz.; sugar candy, 1 oz.; camphor, 1 oz.; alcohol. 600 oz.

- 311. Shellac,  $1\frac{1}{2}$  oz.; resin,  $1\frac{1}{2}$  oz.; alcohol, 20 oz.
- 312. Elemi, 2 oz.; gum benzoin, ½ oz.; alcohol, 20 oz.
- 313. Elemi, 1½ oz.; gum benzoin, ½ oz.; shellac, ½ oz.; alcohol, 20 oz.
- 314 (Retouching and Protective).—Shellac, 12 oz.; sandarac, 12 oz.; resin, ½ oz.; castor oil, 1 oz.; alcohol, 60 oz. Hot varnishes for ferrotypes.
- 315 (Do.)—Dammar, Canada balsam or mastic, 20 grs.; benzole, 1 oz.
  - 316 (Do.)—Bleached lac, 4 oz; camphor, ½ oz.; alcohol, 20 oz.

#### Cold Varnishes for Negatives, etc.:-

- 317. Amber, 1 oz.; chloroform or benzole, 16 oz.
- 318. Japanner's gold size, 1 oz.; benzole, 1 oz.
- 319. (Zapon). Amyl acetate, 10 oz.; pyroxilin, 144 grs.
- 320. Bleached lac, 2 oz.; borax, ½ oz.; dry sodium carbonate 60 grs.; glycerine, ½ drachm; water, 20 oz. Dissolve soda and borax in half the water, and boil with the finely-crushed lac until dissolved, then add the remaining water and the glycerine, set aside for a week or more, and decant.
  - 321. Sandarac, 40 grs.; dammar, 40 grs.; benzole, 1 oz.
- 322. Shellac, 1½ oz; alcohol, 20 oz. Dissolve and add ammonia in very small quantities at a time, shaking well after each addition, until the precipitate first formed is almost, but not quite redissolved. Let the whole rest for a month, and decant.
  - 323. Sandarac, 2 oz.; mastic, \(\frac{1}{2}\) oz.; ether, 25 oz.; benzole, 12 oz.
- 324. Elemi, 1 oz.; chloroform, 6 oz. Shake up with broken glass, let settle, and decant.

### PART IV.

#### UTILISATION OF PHOTOGRAPHIC WASTES.

The useful substances obtainable from these may be classified as follows:—

- 1 -Ether and alcohol from old collodion, etc.
- 2.—Potassium oxalate from spent developers,
- 3. Metallic platinum from
  - a. Spent hot bath platinotype developers.
  - b. Spent cold bath platinotype developers.
  - c. Spent platinum toning solutions.
  - d. Paper wastes.
- 4.-Metallic gold from
  - a. Spent gold toning baths.
  - b. Paper wastes.
- 5.—Metallic silver from
  - a. Spent developers with free silver nitrate (collodion).
  - b. Paper waste.
  - c. Washings of prints, etc , before toning.
  - d Old collodion and printing baths.
  - e. Spoilt emulsions
  - f. Films of rejected negatives.
  - g. Old fixing baths.
- 1. Ether-Alcohol.—To recover these from old collodion it is mixed with dried potassium carbonate and redistilled, about 1 oz. of carbonate being used for every 20 ozs. of collodion.

The carbonate is added for three purposes:—(1.) To convert any free iodine into iodide and iodate, and so prevent it from contaminating the distillate. (2) To neutralise any free acid which might be present, and so hinder the product of compound ethers (3) To dehydrate the distillate by combining with any water which might be present.

The specific gravity of the distillate will indicate by referring to the table given on page 70 the quantities of ether and alcohol it contains, and from this the quantity of ether which must be added to render it suitable for making collodion can be at once inferred

By distilling the mixture very slowly, and at as a low a temperature as possible, the ether will pass over first mixed with very little alcohol. The separation is conveniently carried out by receiving

the distillate into a vessel containing a hydrometer or a '74 specific gravity bead and stopping the operation as soon as it is seen that the spec. gravity begins to rise.

Practically, however, it is preferable to distil off the mixture of ether and alcohol, and then render it suitable for subsequent use by adding ether to it.

Methylated spirit, which has been employed for drying plates, emulsions, etc., can be easily dehydrated by shaking it up with dried potassium carbonate. When the carbonate is seen (usually after two days) to have dissolved to an oily liquid which sinks to the bottom of the vessel, the alcohol may be decanted or syphoned off. It is true that this simple method of dehydration renders the alcohol slightly alkaline owing to the trace of water still present dissolving some of the potassium carbonate, but this does not in the least interfere with its subsequent utilisation for dessicating purposes, although, of course, it renders the alcohol quite unfit for making collodion. If the alcohol is required pure and anhydrous it may be rectified in the usual way (vide page 26).

2. Potassium Oxalate from Spent Potassio-ferrous Oxalate Developers.—To get rid of the iron which these contain a saturated aqueous solution of potassium carbonate is added to the liquid until a precipitate ceases to form. By this means the iron is thrown down as ferrous and ferric hydroxides, potassium oxalate passing into solution. The filtrate, which should not give a blue precipitate with potassium ferrocyanide, is exactly neutralised with oxalic acid and evaporated to dryness, when pure potassium oxalate will be obtained.

Spent hot bath platinotype developers can, after separating out the platinum, be worked up in the same way (vide 3a).

3a. Platinum from Hot Bath Platinotype Developers.—Some of this is usually found at the bottom of the containing vessel as a black powder, and the remainder can be precipitated as such by boiling the liquid with a little ferrous sulphate, which, reacting upon the potassium oxalate, yields potassio-ferrous oxalate, and this at once reduces any platinum in solution to the metallic state. About an ounce of a saturated solution of ferrous sulphate will be sufficient for every 20 ounces of developer. If any crystals are present at the bottom of the bottle containing the solution, these are re-dissolved by heat, the whole boiled for 15 minutes with the ferrous sulphate solution filtered, and the filtrate treated as in 2.

The precipitated platinum is freed from iron by being boiled with strong hydrochloric acid, well washed with water, and dried or converted into chloro-platinic acid by dissolving it whilst still moist in aqua regia.

3b. Platinum from Cold Bath Platinotype Developers.—Practically the whole of the platinum will be found in this case at the bottom of the vessel, the trace remaining in solution being recoverable

by 3a. As platinum obtained from this source contains mercury, it is well to heat it to redness for some time (after having freed it from iron in the usual way) to get rid of this substance.

The filtrate from the platinum is in this case of such small bulk that it is scarcely worth while attempting to utilise it, particularly as it contains potassium phosphate, and must in consequence be subjected to special treatment.

3c. Platinum from Toning Solutions.—These will, if boiled with potassio-ferrous oxalate, yield the metal, accompanied by traces of iron, from which it can be freed in the usual way.

3d. Platinum from Paper Wastes -- If these are platinotypes, either hot, cold and printed out they are burnt as described in 5b, and the ash so obtained is first heated to redness for some time, in order to get rid of any traces of mercury (this may be omitted if only hot bath residues are being worked up), then boiled with strong hydrochloric acid, to get rid of iron, and finally converted into chloro-platinic acid with aqua regia.

If the wastes consists of silver prints toned with platinum these are boiled (after having been burnt) with nitric acid, to extract the silver and the residue treated as above It is not, however, as a rule, very profitable to treat paper residues in this way (vide 4b.)

4a. Gold from Toning Baths.—These are evaporated down to small bulk, and then boiled with ferrous sulphate, about 1 oz of the salt being used for every 5 ozs. of bath, when the gold will be precipitated as such. The precipitate is then boiled with strong. hydrochloric acid, to get rid of iron, and dissolved in aqua regia.

A good deal of the gold present in old toning baths is thrown down as a brown powder at the bottom of the containing vessel. This may be filtered off, or the whole may be at once treated with ferrous sulphate, as already described.

4b. Gold from Paper Wastes—The gold in these may be recovered by keeping them separate, and treating the ash with nitric acid, so as to dissolve out the silver. Practically, however, this does not pay (vide 5b), such residues being reduced with the silver ones, when the trace of gold present alloys with the silver, and is either allowed for by the bullion dealer, or remains as a residue, when the metal is dissolved in nitric acid.

If it is desired to convert the brownish precipitate of gold into the usual yellow form it may be mixed with half its weight of sodio-potassium carbonate and a little borax, and heated to intense

redness in a suitable furnace.

Silver from Wastes.—In practice the silver is collected as chloride, bromide, iodide, sulphide and impure metal, and all the residues having been mixed together are reduced at one and the same

The first step is to grind all the perfectly dry residues (vide ante) to an impalpable powder, every pound of which is then mixed with half a pound each of dried sodium and potassium carbonate. This mixture must be made in a large mortar, as it is essential that it should be homogeneous throughout.

To effect the reduction of the mass a furnace of some kind is necessary. For operations upon quantities of two pounds or so an ordinary fireplace may be made use of by employing a "blower" or sheet of iron, arranged so as to close the whole of the front, the draught finding ingress only through the bars of the grate.

The best fuel to employ is kiln coke, broken up into pieces the size of a pigeon's egg, but ordinary gas coke will answer fairly well.

The mixed residue is placed in a crucible, those known as "salamanders" being excellent for the purpose, and this is arranged centrally in a small coal fire, previously made, so as to occupy half or less of the grate. Pieces of the broken coke are then packed round the crucible, and the blower is placed in position.

After a short time the contents of the crucible will melt and collect at the bottom, and when this occurs more of the mixture is added by means of an iron spoon, care being taken that the crucible is not filled too full, otherwise there will be a risk of the contents boiling over.

When the boiling, due to the escape of carbon dioxide gas, has quite ceased, the contents are kept at a vivid red heat for twenty minutes.

Finally the fire is permitted to die out, and when the whole is quite cold, the crucible is broken, at the bottom of which there will be found, if the operation has been successful, a button of pure silver.

If, as sometimes occurs, the metal is found disseminated through the entire mass, it shows that the heat has been insufficient, in which case the fused residue must be ground up once more, and the whole process repeated. Where gas is available, there is nothing better or cleaner for reducing wastes than the injector furnaces made by Mr. Thos. Fletcher, of Warrington. These are made of all sizes, can be employed on an ordinary deal table, and require no special fittings of any description.

The collection of the separate residues will now be described.

5a. Wet Plate Developing Solutions.—These are placed as soon as done with in a suitable receptacle, at the bottom of which the greater part of the silver will be found as such, and the remainder can be precipitated by adding hydrochloric acid.

5b. Paper Wastes.—These consist of the bibulous paper used for draining plates, etc., filter papers used for baths, clippings of sensitised papers, rejected prints, etc., etc.

The organic matter is destroyed by converting the whole into ashes, which may be done by packing the papers in an ordinary clean fireplace, and setting fire to the whole from the top.

Another method of burning the waste, due to Bothamley, is carried out as follows: A piece of thin sheet iron or tin-plate 26 x 20 inches is bent into a chimney 20 inches high and six inches

square, two inches being allowed for overlap. At four inches from the bottom four holes are made, and through these two iron wires are stretched across the chimney, and serve to support a piece of coarse wire gauze forming the grate. A similar piece of gauze placed over the top of the chimney prevents any fragments being carried away by the draught. Two of the edges of the chimney are slit at the bottom as far as the holes carrying the wires, and the metal is bent outwards to allow free ingress of air. When in use the chimney is placed on an iron plate with upturned edges, which serves to catch any ash that may fall through.

5c.d. Washings of Prints, &c., before Toning.—All water which has served to wash off free silver nitrate is preserved and mixed with hydrochloric acid, when silver chloride will be thrown down. Old collodion and printing baths are similarly treated.

5e.f. Spoilt Emulsions of gelatine and collodion and old films may be utilised by boiling them with strong hydrochloric acid, when the gelatin or pyroxilin will dissolve, leaving the silver free. The liquid should be diluted with a considerable quantity of water, and the precipitate permitted to subside.

5g. Fixing Baths of sodium sulphite are mixed with an excess of hydrochloric acid, when the silver is thrown down as silver chloride.

Baths of hypo or cyanide containing no alum can be mixed with liver of sulphur or ammonium sulphide when the silver is precipitated as silver sulphide, but as this is not wholly insoluble in alkaline sulphides, it is preferable to pass sulphuretted hydrogen (vide page 9) through the liquid until a precipitate ceases to form. If either white or chrome alum has been mixed with the hypo an alkaline sulphide cannot be used, as it would precipitate aluminium or chromium hydroxide with the silver sulphide.

# Alternative Methods of Reducing Silver Residues.

Instead of converting the silver chloride, etc., into metallic silver, all haloid residues are dissolved in hypo, and this, having been mixed with the old hypo fixing baths, is poured over sheets of zinc, which will gradually dissolve, leaving metallic silver mixed with some silver sulphide and free sulphur as a grey powder.

When all the silver has been precipitated (proved by the liquid ceasing to give a black precipitate with ammonium sulphide) the sheets of zinc are removed, any adhering silver scraped off their surfaces and dissolved, after careful washing, in nitric acid.

The mixture of silver nitrate and sulphate so obtained is then treated with a slight excess of barium nitrate, filtered and evaporated down.

Silver chloride can also be reduced to the metallic state by placing it in contact with zinc and dilute sulphuric acid, when the hydrogen liberated from the acid will reduce the chloride with the simultaneous formation of hydrochloric acid. The excess of zinc can be dissolved out with fresh sulphuric acid, and the well-washed residue finally converted into silver nitrate in the usual way.

Silver sulphide can be reduced to the metallic state by adding to it its own volume of the following mixture: Flour of sulphur, 2 parts; dried nitre, 4 parts; fine dry sawdust, 2 parts. The whole is then placed in a crucible, and ignited from the top, when it will burn and leave a button of metallic silver.

#### Large Filters

For treating wastes can be made of circles of coarse calico folded in the usual way, sewn together and fixed in a wooden frame, which, when in use, is placed over a large earthenware basin, etc.

Into the calico funnel the filter paper fits.

If the precipitate is in an acid liquid this had best be of white blotting paper, but if it is merely a question of removing a precipitate from a neutral or nearly neutral, thick, unsized brown paper used for lapping will answer quite as well, care being taken, of course, to select a piece free from holes.

#### Assaying Residues.

To do this weigh out any convenient quantity (say, 100 grains), mix it with its own weight of potassic sodium carbonate, and heat the whole to intense redness for an hour in a crucible. Finally collect and weight the button of silver.

Evidently the residues must be homogeneous throughout, otherwise no clue to the value of the whole can be arrived at. If it is thought that the sample contains gold, about half a drachm of the silver obtained from it can be sent to the nearest assay office with instructions to make a parting assay. This will cost 1s. 6d., and will show the quantity of gold present.

The money value of silver at any particular time is found in any of the daily papers where the market price of fine bar silver (always containing 92 5 % of precious metal) is quoted, and from this the value of silver of any standard can be calculated by simple proportion.

### PART V.

#### QUANTITATIVE CHEMICAL ANALYSIS.

#### CHAPTER I.—APPARATUS AND PRELIMINARIES.

Quantitative analysis is that branch of practical chemistry which treats of the processes by which the actual quantity of any constituent present in a compound is determined.

It is sub-divided into volumetric and gravimetric analysis. By gravimetric analysis the exact quantity of any particular constituent present is determined by converting it into a chemical compound, which can be accurately weighed, and of which the exact composition is known. Thus, by taking a certain weight of silver nitrate, and adding to it an excess of hydrochloric acid, all the silver present becomes converted into insoluble silver chloride, which can be easily collected on a filter, washed, dried, and weighed. Since silver chloride (AgCl) is known to contain \( \frac{108}{108}, \frac{1}{5} \text{ths of its weight of silver it is clear that by multiplying by this factor the weight of silver chloride experimentally obtained the quantity of silver present in the original silver nitrate is at once found. A gravimetric analysis has, in fact, been made.

But the same final result can be arrived at in a different way. By gradually adding rather dilute hydrochloric acid to silver nitrate, we begin by obtaining the usual white precipitate, but on continuing to add the acid a point is eventually reached at which the silver chloride ceases to form. Now, if the hydrochloric acid had been added from a graduated vessel, so as to enable the exact volume used to be known, and if, moreover, the quantity of acid present in that volume was also known, it is clear that a very simple calculation would enable the quantity of silver present to be arrived at, provided, of course, we had some means of knowing the exact point at which we must cease adding the acid. Such is the fundamental principle of volumetric analysis.

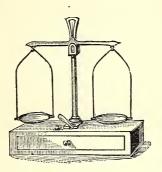
The most convenient system of weights and measures for use in chemical analysis is undoubtedly the French or metrical system. In this the standard of weight is the gram (corresponding to about 15½ grains), the smaller and larger units being obtained by dividing or multiplying this by 10.

The standard of volume is, properly speaking, the litre, or the bulk of 1,000 grams of distilled water measured at 4°C.; but in actual practice the 1000 th part of this, called cubic centimetre, is made use of instead. The cubic centimetre is very vearly 17 minims.

The instruments used in quantitative analysis are the following:

#### Balance.

For analysis this requires to be of a better type and more sensitive than are ordinary scales. The good and cheap balance figured



herewith is made by Messrs. Becker, of Rotterdam, and sold for £1. It carries 100 grams in each pan, and is sensitive to .005 gram with the full load. With such a balance ordinary analyses can be performed with sufficient accuracy for practical purposes. Of course, if research is contemplated, a chemical balance in glass case must be provided, say, one by Wolters or Oertling, costing from £6 to £20.

#### Weights.

As everything depends on these, they must be first class. I have personally for many years past been in the habit of using one of Oertling's 35s. sets, ranging from 50 grams to  $\frac{1}{1000}$ th gram, and this is the set I would recommend.

The greatest care should be taken of the weights, as the slightest rough usage renders them quite worthless. The lid of the box in which they are contained should always be kept tightly closed, and the box itself kept in a bag of chamois.

The weights should never be touched with the fingers, the small forceps provided being always used for transferring them from the box to the scale pan, and vice versâ.

#### Burettes.



These consist of glass tubes provided with a stop-cock at the bottom, and graduated into cubic centimetres. The burette having been filled to the zero mark at the top, the requisite quantity of liquid is permitted to flow out from the stop-cock, and at the conclusion of the experiment simple inspection of the level of the liquid denotes what quantity has been used. A burette or two holding 100 cc., and graduated into fifths of a cc., will be required. The stop-cock should be lightly greased with vaseline when the instrument is in use. A retort-stand provided with a clip serves to support it.

#### Pipettes.



These are bulbs blown on glass tubes, and holding a definite quantity of liquid. Pipettes holding 100, 50, 25, 10, and 5 cc. will be required. Care should be taken in selecting them that the graduating mark on the upper stem is as near the bulb as possible, therwise the instrument will be inconvenient to use.

#### Test Mixer.



This consists of a stoppered bottle of stout glass, holding somewhat more than 1,000 cc., and graduated from the bottom into parts of 5 or 10 cc. capacity. It is intended to dilute liquids to

a given volume. Thus, if it is required to dilute 25 cc. of hydrochloric acid to 1,000 cc., the measured quantity of acid is first placed in the test-mixer, which is then filled up to the mark with water.

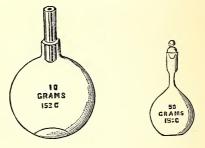
#### Graduated Flasks.



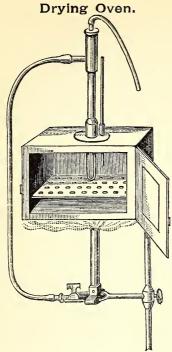
These are sufficiently described by their name, the graduation being effected by a ring etched round the neck of the flask. Flasks of 1,000, 500, and 250 cc. capacity will be required.

#### Specific Gravity Flasks.

These are small bottles, containing when filled to a certain mark a definite weight of distilled water, the graduation being effected in this, as in every other case, at the average summer temperature of 15° C. Two of these will be required—a flask



containing 10 grams water and provided with a thermometer stopper, and another of the Regnault pattern containing 50 grams water. Each of these should be weighed once for all, and the weight noted. Of course, care must be taken that when weighing it the flask is perfectly dry and clean,



This is an arrangement for drying precipitates, etc., at a temperature higher than that of the air. It consists of a chamber of copper or iron heated by gas, and provided with a regulator, which enables the temperature to be maintained at anything from 30°. C to 200° C. A thermometer is also attached to the instrument to show the temperature of the chamber. Failing this somewhat expensive piece of apparatus, many precipitates can be dried perfectly on the lower shelf of an ordinary kitchen oven.

#### Desiccator.



This consists of a glass bottle fitted, as shown, with a cap. The bottom contains strong sulphuric acid, and filters, crucibles, etc., are supported over the surface of the acid by means of pieces of bent wire. The apparatus is intended to hold crucibles, etc., whilst cooling previous to weighing, in order to insure that no atmospheric moisture is deposited on them.

#### Loss of Weight Apparatus.



This consists of a light, small bottle, shaped as in the illustration. It is employed for the analysis of carbonates, etc. Its use will be described further on.

#### Filter Papers.

For gravimetric analysis a special kind is required known as as Swedish. They are of much better quality than the ordinary papers, contain no iron, and leave the faintest trace of ash upon ignition.

#### Water.

Distilled water should invariably be used in every quantitative operation.

Note.—As the burettes, pipettes, and flasks used in analysis are graduated at a certain temperature, care must be taken to bring the liquids measured in them to that temperature, otherwise errors will be introduced.

#### CHAPTER II.—ANALYTICAL OPERATIONS.

#### Weighing.

As in analysis everything depends upon the exactness with which the weighings are performed it becomes necessary to exactly understand how this very important operation is conducted.

To begin with, it must be ascertained that the balance itself is in equilibrium. To do this the pans are dusted with a fine brush, then raised by moving the catch, and caused to oscillate by gently fanning one of them with the hand. If the needle makes equal oscillations on each side of the scale all is well, if not the adjusting vane must be moved right or left until the equilibrium is perfect.

The substance which is to be weighed is never placed on the bare pan, but in a watch glass if a solid, or in a small bottle if a liquid. If the object is to obtain a certain exact weight of any particular substance, a perfectly dry and clean containing vessel is first weighed, and the weight of the substance it is desired to take added to this. This latter weight is then placed in one pan and the vessel in the other, the substance being finally added until equilibrium is restored. Much time is obviously saved by noting once for all the weight of a watch glass and of a thin glass bottle, and keeping these in the drawer of the balance case.

The substance to be weighed is invariably placed in the lefthand pan, and the weights in the opposite one.

The weights themselves are placed on the weight pan methodically, not taken haphazard from the box, as by so doing considerable time is saved. The weights are so arranged in the box as to facilitate this. Thus in Oertling's 50-gram box the pieces are placed in the following order: 50, 20, 10, 10, 5, 2, 1, 1, 5, 2, 1, 1, 05, 02, 01, 01, 005, etc. Suppose the problem is to ascertain the weight of a crucible and contents which we afterwards find to be 49.855 grams. The crucible is placed in the left hand pan, and the 50-gram weight in the right hand one, and the beam released. when it is seen that this weight is too great. It is consequently removed, and the 20-gram piece substituted, this proves too little; we add one of the 10-gram pieces still too little, another 10-gram piece again too little, a five-gram piece too little, a two-gram piece too little, another one-gram piece too little, the second one-gram piece too little, the third one-gram piece too much. We then remove this and substitute the 5-gram piece too little, the 2-gram piece too little, the 1-gram piece too little, the second 1-gram piece too much; remove this and substitute the ·05-gram piece too little, the ·02-gram piece too much, the ·1-gram piece too much, the 005-gram piece correct. Having assured ourselves that the balance is really in equilibrium by causing the pointer to make equal oscillations by gently fanning one of the pans, we arrest the motion of the beam and determine the aggregate value of the weights.

It must be remembered that the motion of the beam must always be arrested whenever an exchange of weight is necessary, otherwise the balance will soon cease to be reliable.

If the object is merely to obtain approximately 10, 5, or 1 gram of a substance, a greater weight than this of the substance is placed in the watch glass or bottle and accurately weighed. A portion is then shaken out into the beaker, etc., in which the analysis is to be performed, and the watch glass or bottle with the remainder of the substance again weighed, when the difference between the two weighings gives the exact quantity taken.

#### Measuring.

Graduated flasks, pipettes, burettes, test mixers, and specific gravity bottles are employed for this purpose.

Graduated flasks are generally used to dilute a liquid to a given volume, or to dissolve a solid so that the solution shall measure a given volume. Thus to dilute a certain volume or weight of hydrochloric acid to a litre (1,000 cc.), we place the known quantity of hydrochloric acid in the litre flask, fill up the latter to the mark with water, and shake it well. Or if the object is to dissolve a given weight of common salt in a litre of water, we transfer this weight to the litre flask, and fill it up to the mark. As in the latter case, unless we remove every trace of common salt from the watch glass on which it has been weighed, we shall have taken too little of the solid, it becomes necessary, after having transferred the bulk of the salt to the flask, to remove the remainder from the watch glass by dissolving it in a little water squirted over the surface of the watch glass from a wash bottle. A funnel placed in the neck of the litre flask will guard against losing any of the substance.

Pipettes are usually employed to obtain aliquot parts of a certain volume of liquid. Thus the 100 cc. pipette gives the 10th of the litre, &c. To fill a pipette the point of the instrument is placed beneath the surface of the liquid, and the latter sucked up by aspirating with the mouth at the other end. When the level has risen above the mark, the mouth is removed and the moistened forefinger of the right hand dexterously applied to the aperture, when on raising the pipette out of the liquid this will remain in it. By very carefully unclosing the aperture a little, the excess can be removed, and when the liquid is at the level of the marked circle the point of the instrument is brought over the beaker, etc., into which the liquid is to be transferred, and the finger removed. Care must be taken in aspirating that the lips are quite dry, and that the tube does not project into the mouth. Neglect of this precaution will probably result in saliva passing down the tube

Burettes are filled by closing the stopcock, and introducing the liquid by means of a funnel placed in the aperture at the top, until it is a little above the zero mark. On opening the stopcock a very little the excess will flow out, the stopcock being closed when the liquid is exactly level with the ring at zero. It is most convenient to take the lowest concavity of the meniscus as the true reading, and care must in any case be taken that the eye is exactly level with the liquid. A piece of silvered mirror held

behind the instrument will facilitate this.

#### Precipitating.

This is carried in quantitative analysis with the object of obtaining some compound in an insoluble form. Evidently care must be taken that the precipitant (as the liquid which causes precipitation is called) is not added in such a way as to cause loss by splashing, nor, generally speaking, is it advisable to employ an excess of it. The process is carried out in beakers, the precipitant being caused to gently flow down the side of the vessel, and the addition of it stopped as soon as it has ceased to produce any effect. It is, generally speaking, advisable to allow the mixture carrying the precipitate to stand several hours before proceeding to collect the latter.

#### Filtering.

This is resorted to for the purpose of obtaining a precipitate in a weighable form. The sides of the glass funnels used in quantitative analysis should be inclined at an angle of 60° exactly, and should be quite free from irregularities. The size of the funnel will depend upon the paper. As a general rule this should be four inches across, necessitating a  $2\frac{1}{2}$ -inch funnel.

The filter paper should be very carefully folded, placed in the funnel, moistened with water, and gently pressed to the sides with the clean finger, so as to cause it to adhere closely. Meanwhile the lip of the beaker carrying the precipitate, having been very lightly greased, a wet glass rod is pressed against it and used (vide page 15) to guide the liquid and precipitate into the funnel, care being taken to allow this to flow down the side, otherwise splashing will almost certainly occur. By holding the beaker with its mouth inclined slightly downwards (the rod being in position against the lip), it is easy by means of a fine stream of water from the wash bottle to transfer almost all the precipitate to the funnel. The fine particles still remaining are wiped out with a tiny piece of filtering paper used on the top of the glass rod and transferred to the bulk already in the funnel. Finally the precipitate is well washed (usually with boiling water) and dried in the drying oven.

#### Burning a Filter.

When quite dry, the filter and contents are placed on a sheet of glazed black paper opened out, and by gently rubbing the sides together between the fingers the bulk of the precipitate is detached and transferred to a crucible, also placed on the sheet of black paper. Finally, the filter paper is rolled up into a spill (taking care not to turn the paper inside out); the extremity of this is grasped in a crucible tongs, and the paper burnt, still over the glazed surface, by holding a Bunsen burner under it, the ash being transferred to the crucible. The fragments of precipitate, etc., on the glazed paper are next brushed into the crucible with a feather, the who'e heated to redness for a couple of minutes, permitted to cool under the desiccator, and weighed when quite cold. The crucibles used in quantitative analysis are of best porcelain, provided with lids, and have a capacity of about half an ounce. Platinum crucibles are also employed, and are exceedingly convenient for many purposes.

#### CHAPTER III.—SPECIFIC GRAVITIES.

The determination of specific gravities is specially useful to the photographer, as enabling him to rapidly determine the actual strength of sulphuric, nitric, hydrochloric and other acids, and of ether and alcohol.

This determination is effected by means of the thermometerstoppered specific gravity bottle when the first three-named acids are in question, the Regnault bottle being available only when dealing with liquids lighter or very little heavier than pure water. To determine the specific gravity of a sample of, say, sulphuric acid, this is cooled (conveniently by immersing a thin flask containing it in a mixture of finely-crushed hypo and its own weight of water) as far below the temperature of the air as possible, the bottle and stopper being meanwhile carefully cleaned, dried and accurately weighed.

When the sample of acid has attained a temperature of about 5°C., the bottle is completely filled with the liquid, the stopper inserted so as to include no air, and the liquid which oozes out from the extremity of the stopper removed by means of a pledget of cotton-wool. In doing this special care must be taken to hold the bottle by the neck so as to avoid heating it.

The bottle and the hollow in the stopper being full of acid the bottle is immersed up to the shoulder beneath the surface of water at 15°C., and permitted to remain there for at least an hour, a collar of lead being slipped over the neck to keep the bottle in position. At the expiration of this time, or when it is seen that owing to the temperature of the acid having ceased to rise the liquid no longer oozes out from the extremity of the stopper, a pledget of cotton-wool is again employed to remove the excess of acid, and the bottle is removed, dried as rapidly as possible and weighed again, taking care that the bare hand does not come in contact with the body of the bottle, otherwise some of the liquid will escape, and the determination will be faulty.

From the weight so obtained that of the empty bottle is deducted, and the difference divided by 10 (as the bottle contains 10 grams of water) gives the specific gravity, from which, by the aid of the tables given in Part II., the actual strength is inferred.

To use the Regnault bottle the liquid (say, alcohol or ether) is again cooled down to about 5°C., and the bottle filled at that temperature up to the mark on the neck. This done, it is immersed in water at 15°C., until the level of the liquid in the neck has ceased to rise. When this occurs a fine pipette, made by drawing out a bit of glass tubing, is employed to remove the excess of liquid, the stopper is inserted, and the whole removed from the water, dried and weighed. This weight, minus the weight of the empty bottle, and divided by fifty, gives the specific gravity of the liquid. In this case no special care need be taken to avoid heating the bottle with the hand, as the liquid cannot escape. This form of bottle is vastly more manageable than the first one, but cannot, unfortunately, be employed (at least with the balance recommended) for heavy liquids owing to its relatively large size. As specific gravity bottles are often incorrectly graduated, it is a useful exercise to determine experimentally the exact weight of distilled water they contain at 15°C., and, if found to differ from that stated, this weight is used as a divisor instead of that marked on the bottle. In determining the weight of the empty bottle it is necessary that it should be perfectly clean and dry. To dry it rapidly after having washed it out with water, fill it with alcohol and let it drain, then with ether and let it drain again. Finally,

warm it very gently and aspirate air through the interior by means of a glass tube, when it will be dry in a few minutes.

It is not, however, essential that the bottle be dried for each successive determination. All that it is necessary to do is to rinse it out two or three times with the liquid whose specific gravity is being determined. This will get rid of practically the whole of the water.

It must not be forgotten that if the liquids whose specific gravities are being determined contain matters in solution the results will be untrustworthy. With acids in such a case we must have recourse to volumetric analysis (vide Chapter IV) alcohol, however, it is possible to remove these matters by distillation, taking a given volume of the alcohol to begin with, pushing the distillation almost to dryness, and diluting the alcohol so obtained until it measures its original volume, all measurements being made at 15°C. The specific gravity of the mixture of alcohol and water will give by reference to the tables the quantity of alcohol in the original. Thus, if it was required to determine the percentage of alcohol in a sample of varnish known to be made up of alcohol and gums only, without any oil of lavender or other volatile matters, the varnish would, to begin with, have to be cooled (or warmed) to 15°C., and, say, 100 cc. of it measured at that temperature by means of a pipette into a flask connected with a Liebig's condenser, the free end of which was placed over a 100 cc. flask. On heating the flask the alcohol would escape and collect in the receiver, the distillation being continued almost to dryness. Finally, the receiver would be cooled to exactly 15°C. and water added to the liquid in sufficient quantity to bring it up to the mark, and the specific gravity of the mixture determined in the usual way.

Exactly the same process could be applied to the distillate from collodion emulsions containing ether and alcohol, making use of the table given on page 70 to ascertain the percentage of ether and of alcohol present. Hydrometers and specific gravity beads are often used instead of specific gravity bottles, but their indications, unless in very experienced hands, are not so reliable.

For certain purposes (vide Part IV.) specific gravity beads are, however, very useful. They consist of small hollow closed glass beads, weighted so as to be balanced in a liquid of a certain specific gravity, and sinking consequently in a lighter, and floating in a heavier, one.

#### CHAPTER IV.—ACIDIMETRY.

When caustic soda and hydrochloric acid react they do so in accordance with the equation NaOH + HCl = NaCl +  $\rm H_2O$ , forty parts by weight of the alkali combining with 36.5 parts by weight of the acid to yield two perfectly neutral products, viz.: common salt and water.

Certain substances, like methyl orange, or phenol phthalein, are used in acidimetry and alkalimetry to *indicate* the presence of an excess of acid or alkali, and are on that account termed *indicators*; thus, methyl orange in its normal state is orange, but it becomes a light yellow in presence of free acids, whilst alkalies restore its original orange colour.

Just as with hydrochloric, so with nitric, acetic, formic and hydrobromic acids; one molecular weight of caustic soda (forty parts by weight) neutralising one molecular weight of each of

these acids.

With sulphuric acid, however, the equation is  $2\text{NaOH} + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$ , and similarly with oxalic and tartaric acids, so that, in this case, one molecular weight of the alkali will neutralise *half* a molecular weight of each of the acids mentioned.

With citric acid the equation becomes  $3\text{NaOH} + \text{H}_3\text{C}_6\text{H}_5\text{O}_7 = \text{Na}_3\text{C}_6\text{H}_5\text{O}_7 + 3\text{H}_2\text{O}$ , one molecular weight of alkali neutralising, in this case, one-third of a molecular weight of acid. All these

facts are embodied in the following table:-

#### ACIDIMETRICAL TABLE.

27	Formula.	Fanivalent	Weight in grams equive
Name.	rormuia.	Equivalent.	Weight in grams equiva- ent to icc. of normal alkali-
Hydrochloric acid	HCl	36.5	•0365
Hydrobromic acid	HBr	81 0	.0810
Nitric acid	$\mathrm{HNO}_3$	63 0	·0630
Acetic acid	$\mathrm{HH_{3}C_{2}O_{2}}$	60.0	.0600
Formic acid	$HHCO_{2}$	46 0	·0460
Sulphuric acid	$H_2SO_4$	49.0	·0490
Oxalic acid	$\mathrm{H_{2}C_{2}O_{4}}$	45.0	.0450
Tartaric acid	$H_{2}^{2}H_{4}C_{4}O_{6}$	75.0	·0750
Citric acid	$H_{3}^{2}H_{5}^{4}C_{6}^{4}O_{7}^{3}$	64.0	·0640

A normal alkaline solution is one which contains a molecular weight in grams of the alkali in a litre of water, and to make it with caustic soda we should (theoretically) take 40 grams of caustic soda, dissolve this in water, and dilute the solution until it measured a litre. Then to analyse, say, hydrochloric acid, we would take any convenient quantity of the acid (let us say 365 grams), add to it a few drops of an aqueous solution of methyl orange (vide Part III.), and deliver our normal hydrochloric acid into the solution until the orange colour was just changed to yellow. If the hydrochloric acid was perfectly free from water (a condition, of course, never met with), we should find that 10 cc. would be required (since the weight of a caustic soda in 10 cc. = '40, and this is equivalent to 365 of hydrochloric acid), and we should therefore pronounce the hydrochloric acid to contain 100 % of true acid. Practically less than 10 cc. of hydrochloric acid would be required. and clearly ten times the actual number of cc. would represent the actual percentage of hydrochloric acid in the sample.

Practically caustic soda is never pure, so we begin by making the solution too concentrated, and then dilute it down to the proper

strength.

To do this we take fifty grams of that substance, dissolve it in a little water, and dilute the solution until it measures a litre, and fill a burette with it.

Meanwhile 10 cc. of normal hydrochloric acid (vide Chapter V.) are measured out, mixed with a little methyl orange, and the caustic soda added to this until the original orange colour is just restored. If our caustic soda was exactly normal evidently 10cc. would be required for this, but as we have purposely made it too strong, we shall find that less than 10 cc. will suffice.

Let us assume that the exact number is found to be 6.8 cc., then it is clear that if this volume had been diluted with water so as to measure 10 cc., it would then have been equivalent cc. per cc. to the normal hydrochloric acid, and we must consequently dilute it until it is to that extent.

To effect this we place in the test mixer 680 cc of the caustic soda solution, and fill up the vessel to the mark with water, transferring the result to a clean and dry bottle, and labelling it "Normal caustic soda."

Having once prepared a litre or so of normal caustic soda, the analysis of any acid becomes a very simple matter. It is only necessary to take a certain weight of it (about 2 grams), dilute it with water or dissolve it, if solid, in that liquid, add a few drops of an aqueous solution of methyl orange for hydrochloric, hydrobromic, nitric, and sulphuric acids, or of an alcoholic solution of phenol phthalein if for the others, and add the caustic soda from the burette until the point of neutrality is reached. Then the number of cc. of caustic soda used multiplied by the weight in grams of each acid equivalent to each of these (column iv. of table) gives the weight of acid in that particular sample, and from that the percentage of acid can be calculated by a simple proportion.

#### CHAPTER V.—ALKALIMETRY.

Just as by means of normal alkali we can estimate volumetrically the strength of any acid, so normal acid serves to estimate the strength of any alkali, and by the same reasoning as in the former case we arrive at the following:—

#### ALKALIMETRICAL TABLE.

Nam	e.	Formula.	Equ	ivalent.	$\epsilon$	eight in grams equivalent to c. normal acid.
Ammonium	hydroxide	$NH_4OH$		35		.035
Potassium	,,	KOĦ		56		.056
Sodium	,,	NaOH		40		.040
Ammonium	carbonate	$(NH_4)_{\circ}CO_{\circ}$		48		.048
Potassium	,,	K,CO.		69		.069
Sodium	,,	$\tilde{\text{Na}}_{2}\tilde{\text{CO}}_{3}$		53		.053

To prepare normal hydrochloric acid we take the specific gravity of a sample of pure acid, and having thus ascertained its approximate strength, we take the equivalent of about 40 grams of real acid and dilute this to a litre.

Lei us suppose that we find the specific gravity of our sample of acid to be 1.2; then on referring to the table we see that this corresponds to 40.7% of real acid, i.e., we should have to take 100 grams of this acid to obtain 40.7 grams of real hydrochloric acid. It is more convenient, however, to measure such a large quantity of acid, and remembering that its specific gravity is 1.2, we know that  $\frac{100}{1}$  = 84 cc. (nearly) will weigh 100 grams. We therefore measure out this quantity by means of a burette, and dilute it to one litre. We have still, however, to determine its exact strength. To do this we take exactly .53 grams of pure dry anhydrous sodium carbonate (Howard's can always be relied on), heat it to 100°C. for an hour or so; dissolve it in a little water in a good-sized beaker; add some methyl orange, and deliver in the acid from a burette until the neutral point is reached. Now, had our acid been exactly normal, 10 cc. of it would have been required, but, having made it purposely too strong, we shall find that less than 10 cc. are needed.

Let us assume that the precise number is found to be 8.4 cc. Then, evidently, we must dilute our acid so that 8.4 will measure 10 cc; or to obtain a litre of normal acid we place in the test-mixer 840 cc. of this acid, and fill it up to the mark with water. To analyse any alkali by means of the standard acid, we take a known weight of it (about two grams), dissolve this in a little water, add methyl orange, and run in the standard acid from a burette until the neutral point is reached. Then the number of cc. used, multiplied by the figure given in column iv. of the table, informs us at once what quantity of real alkali was present, and from this the percentage can be easily calculated. Care must be taken when analysing carbonate to add the acid carefully, otherwise there will be a risk of loss by spirting due to the evolution of carbon dioxide gas.

## CHAPTER VI.—VOLUMETRIC ANALYSIS BY PRECIPITATION.

Silver nitrate gives with hydrochloric acid or a soluble chloride an insoluble precipitate of silver chloride AgCl, and with hydrobromic acid or bromides, and hydriodic acid or iodides, it yields insoluble precipitates of silver bromide and iodide (AgBr, AgI).

Silver nitrate gives with potassium chromate a brick-red precipitate of silver chromate, which, however, is only formed after any halogens present have first been converted into insoluble silver haloids.

It is evident from the foregoing that if a solution of silver nitrate is added drop by drop to a solution of, say, sodium chloride, mixed with a little potassium chromate, a white precipitate will gradually fall, and when all the chlorine has been removed, the least excess of free silver nitrate will be indicated by the formation of brick-red silver chromate.

These reactions form the basis of a simple and accurate method of estimating chlorine, bromine, and iodine when present, either in combination with hydrogen or with metals as soluble haloid salts.

The silver solution for this purpose is conveniently a decinormal one made by dissolving 17 grains of pure re-crystallised silver nitrate in water, and making up the solution to a litre. Every cc. of this solution will contain '017 grains of silver nitrate, equivalent to '0108 grains of silver, and is used in conjunction with the table given below.

#### Hydracids and Soluble Haloid Salts.

Weight in grams, Equivalent to 1 cc. of Decinormal Silver Nitrate Solution. Name. Formula. Equivalent. Hydrochloric acid HCL 36.5 .00365 .0081 Hydrobremic acid HBr 81 128 Hydriodic acid HI  $\cdot 0128$ Potassium Chloride 74.6.00746 119  $\cdot 0119$ Bromide Todide 166  $\cdot 0166$ Sodium Chloride 58.5 .00585 .0103 Bromide 103 ,, Todide 150 .0150Ammonium Chloride 53.5.00535 98 .0098 Bromide Iodide ·145  $\cdot 0145$ Lithium Chloride 42.5  $\cdot 00425$ 87. .00870 Bromide ,, Iodide 134 .0134 Strontium Chloride 79.3 $\cdot 00793$ Bromide 123.8 ·01238 Todide 170.8.01708Calcium Chloride 55.5 00555.0100 Bromide 100 Iodide  $\cdot 0147$ 147 Cadmium Chloride 91.5 .00915Bromide 136  $\cdot 0136$ ,, Iodide 183 -0183Magnesium Chloride 47 5 .0047592. ·0092 Bromide Iodide 139 ·0139 Zinc .00681 Chloride 68.1Bromide 112.6 $\cdot 01126$ ,, Iodide 159.6  $\cdot 01596$ ,,

To analyse any of the solids mentioned in the table about one gram is weighed out, dissolved in water, and the solution made up to 250 cc. One-tenth of this volume (25 cc.) are then measured out with a pipette mixed with a few drops of a saturated solution of potassium chromate, and the decinormal solution of silver nitrate added from a burette until a red precipitate of silver chromate begins to appear. Ten times the number of cc. of silver nitrate used, multiplied by the factor given in the fourth column of the table, will then give the actual quantity of haloid salt present in the sample taken for analysis. In estimating the hydracids a given weight (again about one gram) is taken, diluted with water mixed with a few drops of methyl orange, and exactly neutralised with pure caustic soda. The liquid is then diluted to 250 cc., and 25 cc. of it are mixed with potassium chromate and treated as above.

Note.—Of course if the salts, etc, are not pure, the results will be untrustworthy. Thus, if potassium iodide containing bromide were being analysed, the bromide would be estimated as iodide, thus making the salt appear to contain more iodine than it actually did.

# CHAPTER VII.—VOLUMETRIC ANALYSIS BY PRECIPITATION (Continued).

Silver nitrate gives with sodium chloride a white precipitate of silver chloride, whilst sodium nitrate remains in solution, thus,  $AgNO_3 + NaCl = AgCl + NaNO_3$ , and from the equation it is evident that 58·5 part by weight of common salt are equivalent to 108 parts by weight of silver.

If, then, a solution was made containing 58.5 grams of common salt per litre, every cc. of this would be equivalent to .170 grams of silver nitrate, or 108 grams of silver. Practically, however, the common salt is made up as a decinormal solution, i.e., one containing 5.85 grams per litre, and each cc. of which is consequently equivalent to 0108 grams of silver. At first sight it would appear possible to employ such a solution volumetrically by adding it directly to a given weight of the silver salt to be analysed. Practically, however, it is not easy to observe the end of the reaction, for which reason the decinormal solution of common salt is used conjointly with the decinormal solution of silver nitrate described in Chapter VI. As these solutions are both decinormal, it is evident that they should react upon each other cc. for cc., so that if to any solution containing silver an excess but known volume of the common salt solution is added, all the silver will be thrown down, and the excess of common salt remaining can then be estimated by adding a drop or two of potassium chromate, followed by the decinormal silver solution, and the number of cc. of this taken from the number of cc. of common salt originally added gives the volume actually used up.

Soluble salts of silver are analysed and the quantity of precious metal in coin, etc., is estimated by these two solutions in the following way:—

To estimate the purity of silver nitrate a given weight, say 5 to 1 gram, is dissolved in water, and a volume of decinormal sodium chloride added, more than sufficient to precipitate the silver. In this case, taking 1 gram as the quantity weighed, we should require (since every cc. of common salt solution is equivalent to 0.017 grams of silver nitrate) 0.017 = 60 cc. (nearly) of common salt solution. We add, therefore, more than this, or 100 cc. from a pipette, and add to the liquid without filtering off the precipitated chloride a few drops of potassium chromate, and then drop in the silver nitrate until the silver chromate begins to form. Let us assume that 54 cc. of the silver solution were required. Then clearly 100 - 54 = 56 cc. of common salt were used up in precipitating the silver, and since each of these is equivalent to 017 grams of silver nitrate, our sample actually contained  $0.017 \times 56$ = .952 grams of the pure salt, or 95.2 per cent. The actual quantity of silver nitrate present in bath solutions can be similarly estimated. To save calculation a little pipette of one drachm capacity is made from a piece of glass tubing, and this is employed to measure out that quantity of bath. To this is added 50 cc. of decinormal common salt, then a few drops of chromate, and finally decinormal nitrate, until the excess of salt is completely precipitated. Let us assume that 22 cc. of the latter were necessary. Then 50 - 22 = 28 cc. of common salt were used, corresponding to  $.017 \times 28 = .476$  grams, or  $.476 \times$ 15.5 = 7.378 grains per drachm, or 59.024 grains per ounce. As the silver solutions used in photography are seldom or never stronger than 80 grains per ounce, the 50 cc. of common salt will always be found sufficient to precipitate all the silver in a drachm of solution and leave at the same time an excess of salt. If the bath solution is acid it must be exactly neutralised with pure sodium carbonate after precipitating the silver with the common salt.

To analyse silver coin, jewellery, etc., a definite quantity, say about '5 gram, is taken, dissolved in nitric acid, the solution exactly neutralised with sodium carbonate, 50 cc. of common salt solution added to this, and the estimation proceeded with in the usual way, each cc. of common salt solution corresponding to '0108 grams of metallic silver.

### CHAPTER VIII.—VOLUMETRIC ANALYSIS BY OXIDATION.

When substances which absorb oxygen, like ferrous salts or oxalic acid, are brought in contact with substances which, like potassium permanganate, contain an available store of that element, an interchange takes place, the readily oxidisable substance becoming oxidised at the expense of the permanganate.

This latter dissolved in water yields an intensely pink solution, and as, fortunately, manganese sulphate, the product of its deoxidation, is practically colourless, we can base on these facts a very generally applicable and accurate system of volumetric analysis.

As recrystallised oxalic acid ( $H_2C_2O_4$ · $2H_2O$ ) is easily procured quite pure, it is convenient to begin by preparing a solution con-

taining 6.3 grams per litre of it.

Since in its action upon potassium permanganate, oxalic acid splits up thus,  $\underline{K_2Mn_2O_8} + 5(\underline{H_2C_2O_4 \cdot 2H_2O}) + 3\underline{H_2SO_4} =$ 

10CO<sub>2</sub> + 18H<sub>2</sub>O + 2MnSO<sub>4</sub> + K<sub>2</sub>SO<sub>4</sub>, it is evident that a solution of permanganate containing 3·16 grams per litre will correspond cc. per cc. to the standard oxalic acid.

To prepare the permanganate solution, four grams of the commercial salt are dissolved in a little water, and the solution diluted

to a litre.

Meanwhile 10 cc. of the standard oxalic acid are measured out into a beaker, mixed with 5 cc. dilute sulphuric acid, and heated almost to boiling, and the permanganate solution added from a burette until the pink colour is permanent. The operation must not be hurried, as the colour disappears somewhat slowly, becoming first brown, then yellow, and finally colourless. When the pink colour of the permanganate is seen to be permanent, the number of cc. employed is noted, which, as the solution has been purposely made too strong, will be less than 10. Supposing it to be 8-4 cc., then it is evident that a solution of permanganate, equivalent cc. per cc. to the oxalic acid, will be got by measuring out 840 cc. of the permanganate in the test mixer, and filling it up to the 1,000 cc. mark with water.

These solutions are employed to analyse the substances mentioned in the following table:—

### Table for use with Standard Permanganate and Oxalic Acid.

	Weight in	grams,
	Equivalent	to 1 cc.of
Name.	Formula. Standard S	olution.
Oxalic acid	$H_{2}C_{2}O_{4}+2H_{2}O$	.0063
Normal potassium oxalate	$K_2C_2O_4$	.0083
" ammonium oxalate	$(NH_4)_2C_2O_4$	$\cdot 0062$
" sodium oxalate	$Na_2\tilde{C}_2O_4$	$\cdot 0067$
Ferrous sulphate	$FeSO_4 + 7H_2O$	$\cdot 0278$
Ferrous ammonium sulphate	$FeSO_4 + (NH_4)_2SO_4 + 6H_2O$	$\cdot 0392$
Gold chloride	AuCl <sub>3</sub>	.0101
Sodium thiosulphate (hypo)	$Na_{2}S_{2}O_{3} + 5H_{2}O$	$\cdot 0031$
" sulphite	$Na_2SO_3+7H_2O$	$\cdot 0126$
Potassium metabisulphite	$K_2 \bar{S}_2 O_5$	$\cdot 00555$
Sulphurous acid	$H_2SO_3$	$\cdot 0041$
=		

The equation representing the decomposition of oxalic acid by potassium permanganate has already been given, and the change suffered by the oxalates is exactly similar, these being first converted into oxalic acid by the addition of dilute sulphuric acid.

To analyse oxalic acid or the oxalates about 1 gram of the salt is taken, dissolved in water, the solution made up to 250 cc., and 25 cc. (one-tenth of the whole) transferred to a beaker, mixed with an excess of strong sulphuric acid heated to boiling, and the standard permanganate added from a burette until the pink colour is permanent. Then ten times the number of cc. used multiplied by the factor in the third column will give the quantity of pure substance actually present.

Ferrous sulphate and potassium permanganate react as follows—  $10(\text{FeSO}_4 + 7\text{H}_2\text{O}) + \text{K}_2\text{Mn}_2\text{O}_8 + 8\text{H}_2\text{SO}_4 = 5\text{Fe}_2(\text{SO}_4)_3 + 2\text{MnSO}_4 + \text{K}_2\text{SO}_4 + 15\text{H}_2\text{O}$ , the change brought about with ferrous ammonium sulphate being similar.

To analyse these two salts about 1 gram is taken dissolved in dilute sulphuric acid (1 to 10), and the permanganate added as before, the final calculation being also made in the same way.

Gold chloride is decomposed by oxalic acid in accordance with the equation,  $3\mathrm{H}_2\mathrm{C}_2\mathrm{O}_4 + 2\mathrm{H}_2\mathrm{O} + 2\mathrm{AuCl}_3 = 6\mathrm{CO}_2 + 6\mathrm{HCl} + 2\mathrm{Au}$ , and clearly if to a given weight of gold chloride we add standard oxalic acid in quantity more than sufficient to precipitate all the gold, the excess present will in its turn decompose a certain quantity of standard permanganate, and the number of cc. actually used up by the gold will be the total number added less the number of cc. of permanganate necessary to decolourise these.

To carry out the analysis of gold chloride about ·1 gram of it is taken mixed with 25 cc. of standard oxalic acid, and the mixture kept in a warm place for 24 hours. At the expiration of this time all the gold will be precipitated, and a certain quantity of oxalic acid used up. It remains merely to acidulate the liquid with sulphuric acid, and add permanganate to it until the pink colour is permanent, when the number of cc. of oxalic acid originally employed, minus the number of cc. of permanganate used to estimate the excess, will give the quantity of oxalic acid used to precipitate the gold, from which the quantity of gold chloride present can at once be inferred.

Gold coin or jewellery can be estimated similarly by dissolving about 1 gram of it in aqua regia, evaporating to complete dryness, redissolving in water, adding 50 cc. of oxalic acid, and proceeding as above. The quantity of gold in toning solutions can also be determined by means of oxalic acid and potassium permanganate. To save calculation, a small pipette holding a drachm is used to measure out that quantity of solution, and 25 cc. of oxalic are mixed with it, the whole being set aside for 24 hours, at the expiration of which time the excess of oxalic acid is estimated with permanganate, when the difference multiplied by 0101 and by 15.5 (grains per gram) will give the number of grains of gold chloride in the drachm of solution, and this multiplied by eight will give grains per ounce.

Potassium permanganate oxidises sodium thiosulphite, sulphite of sodium or potassium, or sulphurous acid, provided these are

neutral or alkaline, a certain quantity of permanganate being used up in so doing, becoming converted, in fact, into manganese

hydroxide or manganese sulphate.

If now an excess of oxalic acid followed by sulphuric acid is added to the liquid some of this will be oxidised by the residual permanganate, and the sulphuric acid will dissolve the manganese hydroxide, etc., to an almost colourless liquid.

The residue of oxalic acid in this liquid can then be determined in the usual way with permanganate, and will, of course, correspond to the quantity of permanganate originally used up to

oxidise the thiosulphate, etc.

The following example will serve to make matters clear:— 100 cc. of the standard permanganate would normally suffice to oxidise 100 cc. of the standard oxalic acid, but if we begin by mixing the permanganate with a quantity of sodium thiosulphate (hypo) insufficient to reduce the whole of it a certain number of cc. will be used up in the oxidation of this.

Let us assume that 55 cc. are so used up. Then clearly 100-55=45 cc. of free permanganate remain. If now we add to the liquid 100 cc. of standard oxalic acid followed by sulphuric acid, 45 cc. of these will be decomposed by the 45 cc. of free permanganate present, leaving 100 - 45 = 55 cc. undecomposed. On adding standard permanganate to the nearly colourless liquid clearly 55 cc. of it will be required to decompose the 55 cc. of oxalic present, and this number is the same as the number of cc. of permanganate originally employed to oxidise the thiosulphate.

To carry out the analysis about one gram of hypo, two grams of metabisulphite, or four grams of sulphite, are weighed, dissolved in water, the solution made up to 250 cc., 25 cc. of it taken, made alkaline with caustic soda, mixed with 100 cc. of permanganate, and boiled for a couple of minutes. 100 cc. of standard oxalic acid are then added, followed by 10 cc. of dilute sulphuric acid, and the whole again boiled, standard permanganate being finally added from a burette to the boiling liquid. The number of cc. of this necessary to produce a permanent pink colour, multiplied by the factors given in third column and by ten, gives the quantity of sulphite, etc., in the original sample.

With sulphurous acid about five grams of it are weighed, made alkaline with caustic soda, and treated as above. The following equations represent the final result of the oxidation of these

substances with potassium permanganate: -

Sodium thiosulphate  $-5(Na_2S_2O_3 + 5H_2O) + 4K_2Mn_2O_8 +$  $7H_2SO_4 = 5Na_2SO_4 + 4K_2SO_4 + 8MnSO_4 + 12H_2O_5$ 

Sodium sulphite -  $5(Na_2SO_3 + 7H_2O) + K_2Mn_2O_8 + 3H_2SO_4$  $= 5 \text{Na}_2 \text{SO}_4 + \text{K}_2 \text{SO}_4 + 2 \text{MnSO}_4 + 10 \text{H}_2 \text{O}.$ 

Potassium metabisulphite -8K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> + 2K<sub>2</sub>Mn<sub>2</sub>O<sub>8</sub> + H<sub>2</sub>SO<sub>4</sub>  $= 7K_2SO_4 + 4MnSO_4 + H_2O.$ 

Sulphurous acid  $-5H_2SO_3 + K_2Mn_2O_8 = 2MnSO_4 + K_2SO_4$  $+ 2H_2SO_4 + 3H_2O.$ 

### CHAPTER IX.—GRAVIMETRIC ANALYSIS BY LOSS OF WEIGHT.

When sulphuric acid reacts upon ammonium, sodium, or potassium carbonate these are decomposed with the evolution of carbon dioxide gas, and the formation of the corresponding sulphate. The latter, being non-volatile, remains behind, but the carbon dioxide escapes, mixed usually with some vapour of water. From the equations

$$(NH_4)_2OO_3 + H_2SO_4 = (NH_4)_2SO_4 + H_2O + CO_2$$
  
 $Na_2CO_3 + H_2SO_4 = Na_2SO_4 + H_2O + CO_2$   
 $K_2CO_3 + H_2SO_4 = K_2SO_4 + H_2O + CO_2$ 

it is evident that 44 parts by weight of carbon dioxide correspond to 96 parts by weight of ammonium carbonate, to 106 parts by weight of sodium carbonate, and to 138 parts by weight of potassium carbonate respectively.

And if we decompose the carbonates in such a way as to be able to estimate the quantity of carbon dioxide liberated we have a simple and accurate method of analysing them. To carry out the process use is made of the loss of weight apparatus described on page 222.

About 10 cc. of water are introduced into the body of the instrument, and sufficient strong sulphuric acid placed in the middle bulb to just cover the junction of the two tubes. The side bulb is also three-quarters filled with dilute sulphuric acid, taking care to close the stopcock, so as to let no acid into the body. In this condition the whole instrument is wiped dry and clean, and weighed as accurately as possible.

This done, about three grams of whatever carbonate it is desired to analyse is placed in the body of the instrument by removing the stopcock, and the whole again weighed after the stopcock has been replaced. Clearly, the difference between the two weighings gives the weight of carbonate taken for analysis.

Matters having progressed so far, the stopcock connecting the body with the side bulb containing the dilute sulphuric acid is very carefully opened so as to let a single drop of sulphuric acid come in contact with the carbonate. Effervescence at once commences, and the liberated carbon dioxide escapes through the sulphuric acid in the middle bulb, and by so doing is freed from every trace of moisture. From time to time the stopcock is reopened so as to bring more sulphuric acid in contact with the carbonate, care being taken that the action does not become violent, otherwise some vapour of water will also escape. When it is seen that all action is at an end, the apparatus is heated to about 50°C. so as to drive off any carbon dioxide remaining in solution in the water, then permitted to cool perfectly and reweighed, when the difference between the two weighings gives the quantity of carbon dioxide which has escaped, and from which the weight of actual carbonate present in the sample can be readily calculated.

When potassium dichromate is brought in contact with oxalic acid and sulphuric acid the following change occurs— $K_2Cr_2O_7 + 3H_2C_2O_4 + 4H_2SO_4 = K_2SO_4 + Cr_2 (SO_4)_3 + 7H_2O + 6CO_2$ , from which it will be seen that 300 parts by weight of bichromate will liberate 264 parts by weight of carbon dioxide.

A rapid and fairly accurate analysis of potassium bichomate based on the above equation is carried out as follows:—The potassium bichromate to be analysed is very finely powdered, weighed, and mixed with one and a-half times its weight of crystallised oxalic acid, also very finely powdered. The mixture is then placed with about 10 cc. of water in the apparatus previously described, arranged as in the estimation of carbonates, but with strong sulphuric acid in both bulbs, and the whole re-weighed. This done, the sulphuric acid is permitted to gradually come in contact with the mixture, and the remaining operations conducted exactly as in the former case.

At the conclusion the difference in weight gives the carbon dioxide which has escaped, and 365ths of this corresponds to the quantity of pure bichromate in the sample submitted to analysis.

# CHAPTER X.—GRAVIMETRIC ANALYSIS BY LOSS OF WEIGHT (Continued).

Certain metallic substances decompose on being heated, and leave behind the metal they contain either as such or in combination with oxygen.

Thus silver nitrate, gold chloride, and chloroplatinic acid leave a residue of metal on being heated to redness for an hour or so in quantities not exceeding a gram, and the knowledge of this fact enables the analysis of those compounds to be (if pure) performed in the simplest possible way. Thus to analyse silver nitrate we need only take a crucible, weigh it, and put into it about a gram or so of the salt, when on weighing again and taking the difference we have the exact weight of silver nitrate employed. If this crucible is now carefully heated, the temperature being gradually raised to full redness and maintained at that latter point for an hour, the nitrate will decompose, and a residue of metallic silver will remain. When the crucible has cooled completely the crucible and contents are re-weighed and the weight of the empty crucible taken from this, when we obtain at one operation the actual quantity of silver present in the sample.

Gold chloride and chloroplatinic acid can be similarly analysed, but it will, of course, be remembered that this method is only applicable when these substances are unmixed with non-valatile salts such as the nitrates or chlorides of potassium, sodium, etc

Ferric or ferrous oxalates will on being heated to redness leave a residue of ferric oxide thus—

$$Fe_2(C_2O_4)_3 = Fe_2O_3 + 6CO_2$$
.  
 $2FeC_2O_4 + O_3 = Fe_2O_3 + 4CO_2$ .

Similarly uranyl nitrate will become converted into uranic oxide (UO<sub>3</sub>), and this enables these salts to be readily analysed, provided, of course, they also are unmixed with other non-volatile substances.

In carrying out such analyses the substance is heated for, say, an hour, then cooled, re-weighed, and again heated. If the second weighing proves identical with the first, it may be concluded that complete decomposition has been effected. If on being weighed a second time the substance weighs less than it did at first it must be again heated, this being repeated until the weight is constant.

Care must always be taken to heat the substance carefully at the commencement, otherwise loss by projection will occur, and it must not be forgotten to permit the crucible to cool completely before re-weighing it, as a hot crucible appears to weigh considerably less than the same crucible when cold, owing to the currents of heated air buoying it up.

Ignition is also frequently resorted to in others cases. Thus, samples of gelatine yield on ignition a variable quantity of ash, the amount of which gives a very good clue to the quality of the original substance.

Ignition can also be made use of to analyse most nitrates. To carry this out, the nitrate in fine powder is mixed with about six times its weight of washed and ignited sand, or, better still, powdered quartz, and the whole kept at a faint red heat for about half-an-hour, when the loss in weight represents N<sub>2</sub>O<sub>5</sub>.

With potassium nitrate, for instance, the ultimate decomposition may be represented by  $2 \mathrm{KNO}_3 = \mathrm{K}_2 \mathrm{O} + \mathrm{N}_2 \mathrm{O}_5$ , from which it will be seen that the loss of weight multiplied by  $\frac{203}{108}$  gives the quantity of potassium nitrate present in the original.

Potassium chloroplatinite can be analysed by igniting it for some time, or until it ceases to lose weight, when it decomposes into metallic platinum and potassium oxide, which latter can be removed by filling up the crucible in which the ignition has been performed with water, and decanting off the liquid very carefully. On repeating this several times all the potassium oxide will be removed, and after driving off the water by careful evaporation the platinum can be weighed as such. The difference between this weight and the former one gives the potassium as oxide. It must not be forgotten with reference to the two last analyses that potassium oxide is exceedingly hygroscopic, for which reason the crucible must be cooled in the desiccator and weighed with its cover on as expeditiously as possible.

#### Table for Use in Analysis by Loss of Weight.

Substance Analysed.	Formula.	Product Weight.	obtain weight of pure substance in original.
Silver nitrate	AgNO <sub>3</sub>	Silver	$\frac{170}{108}$
Gold chloride	AuCl <sub>3</sub>	Gold	303.5
Chloroplatinic acid	$H_2PtCl_6$	Platinum	412 197
Potass. chloroplatinite		Platinum	437
Ferric oxalate	$\operatorname{Fe}_{2}(\operatorname{C}_{2}\operatorname{O}_{4})_{3}$	Ferric oxide	$\frac{376}{160}$
Ferrous oxalate	$FeC_2O_4$	Ferric oxide	144 80
Uranyl nitrate	$UO_2(NO_3)_2$	Uranic oxide	396 288
Potassium nitrate	KNO <sub>3</sub>	Potassium oxid	$\det \frac{101}{47}$
Sodium nitrate	$NaNO_3$	Sodium oxide	$\frac{85}{31}$

## CHAPTER IX.—GRAVIMETRIC ANALYSIS BY PRECIPITATION.

This method of analysis depends, as already explained, upon the possibility of converting certain elements into insoluble compounds admitting of exact weighing.

The course to be followed is practically the same for one and all, viz., a portion of the substance to be analysed is carefully weighed (two to six grams being taken), dissolved in water in a beaker, and the precipitant added until it ceases to produce any effect. The lip of the beaker having been lightly greased, a glass rod is employed to transfer the precipitate and liquid to a filter paper supported in a funnel, every trace of the precipitate being removed by the means already described.

Lastly, the precipitate is very carefully washed, dried, detached from the filter, transferred to a crucible, and the icinerated filter paper added to it; special care being taken, of course, that none of the precipitate is lost.

The weight of the empty crucible being already known, this is deducted from the gross weight, giving the weight of precipitate present, and from this the quantity of any particular element present in the original compound can be inferred.

As an example, I give the record of an actual analysis of a sample of silver nitrate:—

Weight of watch glass and silver nitrate = 23.485 grams.

""", "", partially empty = 20.120 ",

Weight taken for analysis = 3.365 ",

Converted silver into silver chloride by the addition of hydrochloric acid, and collected this in usual way.

Weight of silver choride = 2.710

Since  $AgNO_3=170$ , and  $AgCl=143\cdot 5$ , this weight of silver chloride corresponds to  $3\cdot 210$  grams of silver nitrate, or the original contains  $\frac{3\cdot 210\times 100}{3\cdot 36\cdot 5}=95\cdot 4$ % of pure salt.

This method can be applied (conversely) to analyse hydrochloric, hydrobromic, or hydriodic acids, or the soluble chlorides, bromides, and iodides, by converting these into insoluble silver haloids.

Soluble ferric salts, such as ferric chloride, etc., are estimated by precipitating the iron as ferric hydroxide  $(Fe_2(OH)_6)$  with excess of ammonia, collecting this on a filter, washing it, etc., converting it into ferric oxide  $Fe_2O_3$  by heating it to redness for fifteen minutes, and weighing it as such. From the weight of ferric oxide obtained, the quantity of pure ferric chloride, etc., can be readily inferred.

Soluble ferrous salts (ferrous sulphate, etc.) are weighed out into a large beaker, dissolved in water, and boiled with nitric acid until they are completely oxidised. This point is reached when a minute drop of the solution taken out on the point of a glass rod ceases to give a blue colour with potassium ferricyanide. When oxidised an excess of ammonia is added, and the subsequent operations conducted as with ferric salts.

Sulphuric acid and sulphates are estimated by precipitating with barium chloride and weighing the insoluble barium sulphate. Care must be taken in this case when estimating sulphates to begin by strongly acidifying the solution with hydrochloric acid and then raising it to boiling, at which temperature it must be kept during the addition of the barium chloride. It is also advantageous to permit the precipitate and the supernatant liquid to remain at rest in a warm place for a few hours previous to filtering, otherwise there is a risk of the very finely precipitated barium sulphate passing through the pores of the filter.

Sulphites are estimated by oxidising a known weight completely by boiling with nitric acid, then precipitating the sulphate so formed with barium chloride, and proceeding as with sulphates. As sulphites almost invariably contain sulphates, the quantity of sulphate present is estimated in a fresh portion of the solid by boiling it with hydrochloric acid, free from chlorine, by which the sulphite is decomposed, any sulphate present remaining unchanged and then precipitating the sulphate in solution by means of barium chloride.

Gold is estimated by boiling the solution for a considerable time with ferrous sulphate, and weighing the precipitated gold as such. When washing the precipitate in this case concentrated boiling

hydrochloric acid is used in the first instance to get rid of the iron, this being followed by water. Care must be taken that no nitric

acid is present, otherwise the results will be inexact.

Chloroplatinic acid is estimated (if perfectly neutral) by adding to the concentrated solution five times its weight of ammonium chloride, dissolved in the least possible quantity of water, followed by a volume of absolute alcohol equal to ten times that of the liquid. After twenty-four hours or more, the yellow crystalline precipitate is collected on a filter (the filtrate itself being employed to remove the last traces of precipitate from the beaker), washed twice with absolute alcohol, dried, transferred with the filter to a crucible, and calcined until fumes cease to escape, when a residue of metallic platinum will remain.

If the solution is acid, it must be nearly, but not quite, neutralised

Multiplier to

with ammonia before adding the ammonium chloride.

### Table for Use in Analysis by Precipitation.

obtain weight of pure substance in Substance Analysed. Formula. Product Weighed. original. Silver nitrate... ... AgNo ... ... Silver chloride...  $\frac{170}{143}$   $\frac{365}{1430}$ Hydrochloric acid HCl ... KCl ... ... Potass chloride ... ... NaCl ... ... Ammonium chloride ... NH₄Cl LiCl ... ... Lithium ,, ... ,, SrCl<sub>2</sub>... ... Strontium Calcium Cadmium Cadmium ,, ... Magnesium ,, ... CdCl2... ... ... MgCl<sub>2</sub> ZnCl<sub>2</sub>... Zinc " ... Hydrobromic acid ... HBr ... ... Silver bromide... Potassium bromide ... NaBr... NH<sub>4</sub>Br Ammonium bromide ... LiBr... Lithium ,, ... TEE SrBr<sub>2</sub> ... Strontium  $\frac{1238}{1880}$ Calcium Cadmium ... CaBr<sub>2</sub> ,, ... CdBr<sub>2</sub> Magnesium , ... MgBr<sub>2</sub> ... ,, Zinc ... ZnBr<sub>2</sub> Hydriodic acid ... ... HI ... Silver iodide ... Potassium iodide ... ... KI Sodium " ... ... NaI ... Ammonium iodide ... NH<sub>4</sub>I... ... LiI ... Strontium ... SrI<sub>2</sub> ... ... CaI<sub>2</sub> ... Cadmium Calcium ... CdI<sub>2</sub> ... ... MgI<sub>2</sub>... ... 568 126 233 Potass. metabisulphite K2S2O5 ... ... ... 111

### CHAPTER XII.—GRAVIMETRIC ANALYSIS OF EMULSIONS.

These consist of silver haloids, etc., in suspension, in collodion or gelatine, and a qualitative analysis should first be made to ascertain what silver haloids are present. This is done by intimately mixing the dried (gelatine) emulsion with three times its weight of potassium nitrate, and introducing the mixture in small quantities at a time into a red-hot crucible. When all of it has been introduced, a little sodium carbonate is added, and the mass kept in tranquil fusion for some minutes. By this means the silver haloids are converted into alkaline haloids, metallic silver being set free, and on dissolving the mass in water the solution will contain whatever halogens were originally combined with the silver.

The solution so obtained is carefully filtered, evaporated down to small bulk, and divided into three portions.

To the first portion an excess of acetic acid, followed by hydrogen peroxide, is added, when a brown colour will indicate iodine.

The second portion is boiled with potassium dichromate and sulphuric acid, when brownish-red vapours of chloro-chromic anhydride will indicate chlorine. The third portion is diluted somewhat with water, acidulated with a drop or two of sulphuric acid, mixed with starch paste, and about ten drops of fuming nitric acid, when a blue coloration will confirm the result given by hydrogen peroxide. Chlorine water is next added drop and drop to the liquid until this blue colour just disappears (if it has been produced at all); and this is followed by a little more chlorine water and a few drops of chloroform. On shaking up the mixture the bromine set free by the chlorine will, if present, dissolve in the chloroform and colour it brown.

If the emulsion is a collodion one it is first evaporated to dryness, if ether and alcohol are present, and the residue heated for some time with strong nitric acid, and then treated as before. It will be convenient to describe the analyses of these two types of emulsion separately.

#### A.—COLLODION HALOID EMULSION.

- 1. Percentage of Solvent (if liquid).—Weigh a small flask of about 100 cc. capacity, introduce into it about 10 grams of the emulsion and re-weigh. This gives the quantity taken for analysis. Connect the flask to a Liebig's condenser, and distil to complete dryness at 100° C. The specific gravity of the distillate will approximately give the quantities of ether and alcohol present (vide table, page 70), and the difference in the weight of the flask gives the quantity of solvent.
- 2. Percentage of Pyroxilin.—To the residue at the bottom of the flask from (1) or to the dried emulsion (in this case, of course, a weighed portion being taken) add a large excess of concentrated

nitric acid and boil for an hour, adding fresh quantities of acid to replace that evaporated. The pyroxilin is by this treatment dissolved, and the silver haloids remain behind. Finally evaporate off the greater part of the acid, fill the flask with water, transfer the precipitate to a filter and weigh it, when the decrease in weight over the dried emulsion found in (1) gives the pyroxilin.

3. Percentage of Silver Haloids.—If only one haloid is present (silver bromide), the weight of the precipitate left from (2) gives it directly. If iodide is present as well, digest this weighed precipitate for an hour with ammonium hydrate, and re-weigh, when the differences gives the bromide which has been dissolved.

If all three haloids are present the precipitate left from (3) is mixed with three times its weight of equal proportions of potassium and sodium carbonate, and heated to redness for half-an-hour in a rather large crucible. At the conclusion of this time the mass in the crucible is boiled up with water and transferred to a filter, the filtrate being reserved for examination as below. The silver reduced to the metallic state will remain on the filter, and can, as a check, be weighed as such, whilst the haloids will be present in the filtrate as alkaline salts. Of course the silver and crucible must be carefully washed, and all the washings added to the filtrate. The crucible itself should be weighed before the fusion, and the same crucible employed to weigh the metallic silver. By this means any traces of metal adhering to the sides will be estimated and allowed for.

The filtrate is next strongly acidulated with nitric acid, diluted to 300 cc., and divided into three portions of 160 cc. each. These are separately placed in stoppered bottles of about 250 cc. capacity, the halogen in each completely precipitated with silver nitrate, and the three precipitates carefully washed by decantation. The weight of the precipitate in the first bottle, multiplied by three, gives the halogens as silver chloride, bromide and iodide. The precipitate in the second bottle is drained as dry as possible, and the bottle completely filled with a 5% cold solution of potassium bromide, and a solution of potassium iodide of the same strength is placed in the third bottle, and the two bottles set aside for 12 hours. On weighing the precipitates, that in the second bottle multiplied by three gives the equivalent of chlorine as silver bromide (the potassium bromide having converted the silver chloride into bromide), and that in the third bottle, also multiplied by three, gives the equivalents of bromine and chlorine as silver iodide (the potassium iodide having converted both silver bromide and chloride into silver iodide). From these data the following calculation enables the quantities of silver chloride, bromide, and iodide to be calculated:—

Difference between weights of I. and II. × molecular weight of silver chloride

Difference between weights of II. and III. × molecular weight of silver bromide.

Silver bromide =

Difference between atomic weights of iodine and bromine.

Silver iodide = Weight of I., less weights of silver chloride and bromide

- 4. Percentage of Silver as Free Silver Nitrate.—This determination is preceded by a qualitative test made by shaking up a little of the emulsion with ten times its volume of water, filtering off the precipitate and testing the filtrate for silver nitrate with hydrochloric acid. If free nitrate is present it may be estimated by weighing about twenty grams of the emulsion, shaking this up with 250 cc. of water, filtering, washing the precipitate carefully (the washings being added to the filtrate), and precipitating the silver by means of hydrochloric acid.
- 5. Percentage of Free Alkaline Haloid.—In some emulsions this is present (of course, in the absence of free silver nitrate), and may be tested for qualitatively and examined by the converse of (4).

#### B.—GELATINO-HALOID EMULSIONS.

1. Percentage of Gelatine.—If the emulsion is in the form of pellicle, take about ten grams of it, soak in water, dissolve by heat, add a large excess of concentrated nitric acid, and heat for several hours. By this means all the gelatine is decomposed and dissolved in the acid, whilst the silver haloids remain behind. The liquid is next diluted with water, and filtered, and the silver haloids weighed, when the difference gives the gelatine. If the emulsion is on plates or films, weigh these, cut up into strips about four inches long, soak in water for a couple of hours, dissolve by heat, and wash each strip with boiling water. On re-weighing the bare support, the difference gives the weight of emulsion taken for analysis.

The remaining estimations are made exactly as described under collodion.

### C.—GELATIN, OR COLLODION EMULSIONS WITH ORGANIC ACIDS.

The actual percentage of silver can be estimated by the processes described already, and the quantity of *free* organic acid (if any) estimated volumetrically in the liquid obtained by digesting ten grams or so of the emulsion with water.

By digesting a weighed quantity of the emulsion with an excess of normal caustic soda, any silver tartrate or citrate is decomposed and a portion of the soda neutralised. By ascertaining what quantity of sodium citrate, or tartrate, has been formed, the percentage of silver citrate or tartrate present can be readily arrived at.

By digesting a second weighed portion of the emulsion with strong nitric acid, the silver tartrate and citrate are decomposed, and the haloids left behind. These can be then weighed, and further analysed by the methods already described.

In addition to silver haloids, etc., gelatine and collodion emulsions sometimes contain traces of other substances, such as alkaline nitrates, or cyanides, phenol, salicylic acid, tannin, gallic acid, pyrogallol, tea or coffee. To detect these the following reactions may be made use of:—

Alkaline Nitrates.—Soak the emulsion in cold water for 12 hours, filter, evaporate the filtrate to complete dryness, add to the cold residue a fragment of brucine, followed by a drop of strong sulphuric acid, when a red colour will indicate an alkaline nitrate.

Alkaline Cyanide.—Soak the emulsion in cold water for 12 hours, filter, mix the filtrate with a few drops of yellow ammonium sulphide, evaporate to complete dryness, and add to the residue a drop of ferric chloride, when the production of a blood red colour will indicate a cyanide.

Phenol.—Soak the emulsion in strong alcohol for 12 hours, filter, evaporate to dryness, and add ferric chloride, when the production of a purple blue colour will indicate phenol. To another portion a little mercuric chloride may be added, with which phenol gives a yellow precipitate.

Salicylic Acid.—In the absence of phenol this is identified by the violet colour it gives when ferric chloride is added, as in testing for phenol. Salicylic acid does not give a yellow precipitate with mercuric chloride.

Tannin.—This gives a bluish black colour with ferric chloride, and can also be identified by the gelatinous precipitate it gives with a weak solution of gelatine.

Gallic Acid behaves like tannin with ferric chloride, but gives no precipitate with gelatine.

Pyrogallol gives a bluish-green colour with ferrous sulphate, and a red colour with ferric chloride.

Tea or Coffee are detected by adding a little hydrochloric acid and a crystal of potassium chlorate to the aqueous extract, and evaporating the whole to complete dryness. On adding a drop of ammonia to the residue it will become purple, if tea or coffee were originally present.

### APPENDIX.

### Table of the Elements with their Symbols and Atomic Weights.

N1	03T	10/1	Tam	ALS.

	Sym.	At. Wt			Sym.	At Wt.
Hydrogen	H	1		Nitrogen	N	14.01
Chlorine	Cl	35.37		Phosphorus	$\mathbf{P}$	30.96
Bromine	$\mathbf{Br}$	79.75		Arsenic	$\mathbf{A}\mathbf{s}$	74.90
Iodine	I	126.53		Boron	$^{\mathrm{B}}$	$11 \ 00$
Fluorine	$\mathbf{F}$	19.1		Carbon	$\mathbf{C}$	$11 \ 97$
Oxygen	O	15.96		Silicon	$\operatorname{Si}$	28.30
Sulphur	$\mathbf{s}$	31.98				
Selenion	$\mathbf{Se}$	79.00				
Tellurion	${ m Te}$	125.00				
			METALS.			
Potassium	$\mathbf{K}$	39.04		Gallium	Ga	69.8
Sodium	Na	22.99		Manganese	Mn	54.9
Lithium	$\mathbf{Li}$	7.01		Iron	Fe	55.9
Rubidium	Rb	85.2		Cobalt	Co	58.7
Cœsium	Cs	1330		Nickel	Ni	58.6
Calcium	Ca	<b>3</b> 9 9		Chromium	Cr	$52 \cdot 1$
Strontium	Sr	87 2		Molybedenum	Mo	95.8
Barium	Ba	136.8		Tungsten	W	183.5
Beryllium	Be	9.1		Uranium	U	240.0
Magnesium	Mg	24.2		Tin	$\operatorname{Sn}$	1178
Zinc	$Z_n$	$65 \ 1$		Titanium	Ti	480
Cadmium	$\operatorname{Cd}$	111.9		Zirconium	Zr	90.0
Lead	Pb	206.4		Thorium	Th	231.5
Thallium	$\mathbf{T}\mathbf{l}$	203.6		Vanadium	V	51.2
Copper	Cu	$63 \cdot 1$		Antimony	$\mathbf{Sb}$	$121 \cdot 0$
Silver	Ag	107.66		Germanium	Ge	72.0
Mercury	$_{ m Hg}$	$199 \ 8$		Bismuth	$_{ m Bi}$	208.2
Yttrium	Y	89.0		Tantalum	Ta	182.0
Cerium	Ce	139.9		Niobium	Nb	94
Lanthanum	$_{ m La}$	138.0		Gold	$\mathbf{A}\mathbf{u}$	196.8
Didymium	$_{ m Di}$	142.0		Platinum	$\cdot \mathbf{Pt}$	$194\ 5$
Terbium	${ m Tr}$	148.5		Palladium	$_{\mathrm{Pd}}$	106.2
Erbium	$\mathbf{Er}$	166.0		Rhodium	Rh	$103\ 0$
Ytterbium	Yb	173 - 0		Iridium	$_{ m Ir}$	192.7
Aluminium	$\mathbf{Al}$	27.0		Ruthenium	Ru	103.5
Scandium	Sc	44.0		Osmium	Os	194.0
Indium	$_{\rm In}$	113.4				

### English Measures.

#### TROY WEIGHT.

Employed in weighing gold, silver, precious stones, and other costly articles, and in philosophical investigations.

Name.	Symbol.		
Grain	gr	Smallest weight	t.
Pennyweight	dwt	24 grains.	
Ounce	oz	20 pennyweight	ts.
Pound	lh.	19 ounger	

g

Degree ..

### English Measures-(Continued).

APOTHECARIES' WEIGHT.

Employed in	mixin	g medi	cines			
Name.			Symbo			
Grain			gr.			Smallest weight.
Scruple						20 grains.
Drachm			dr. o	r 3		3 scruples.
Ounce			oz. or	: 3		8 drachms.
Pound $\dots$	• •	• •	lb.	• •		12 ounces.
		Avoir	DUPOI	s Wei	GHT.	
Employed in	weigh	ing all	objec	ts of co	omme	rce except medicines,
gold, silver, and	preci	ous sto	nes.			-
Name.		$S_{\mathcal{I}}$	<i>ymbol</i>			
Grain			gr.	• •		Smallest weight.
$\mathbf{Drachm}$	• •	(	dr.			$27\frac{1}{3}$ grains.
Ounce			oz.			16 drachms.
Pound		]	lb.			16 ounces.
Quarter		(	qr.			28 pounds.
Hundredwe	ight	(	owt.			4 quarters.
${f Ton}$		• •	ton	• •	• •	20 hundredweights.
		LINI	EAR N	IEASUR:	E.	
Name.		1	Symbo	ol.		
$ \text{Inch}  \dots$			in.			Smallest length.
$Foot \dots$			ft.			12 inches.

Yard ... 3 feet. yd. . . Fathom fth. 6 feet. . . . . Rod, pole, perch 51 yards. po. Furlong fur. 40 poles. Mile m. 8 furlongs. League ... lea. 3 miles. • •

### .. deg. or ° Liquid Measure.

69½ miles.

Name Symbol. Minim .. Smallest unit. m. Drachm dr. 60 minims. Ounce .. 8 drachms. oz. . . . . Gill gl. 5 ounces. Pint 4 gills. pt. Quart 2 pints. . . qt. Gallon .. gn. 4 quarts.

### Metrical Measures.

Length. Volume. Weight. Millimetre ·001 metre Millilitre (cc) ·001 litre Milligram ·001 gram Centimetre ·01 Centilitre .01 Centigram '01 Decimetre Decilitre Decigram ,, Metre Litre Gram. Decametre 10 ms. Decalitre 10 litres Decagram 10 grams Hectometre 100 Hectolitre Hectogram 100 100 ,, ,, 1000 Kilometre 1000 Kilolitre Kilogram 1000 ,, Myriometre 10,000, Myriolitre 10,000 Myriogram 10,000,,

### Comparison of Metrical with Ordinary Measures.

#### MEASURES OF LENGTH.

	Inches.	Feet.	Yards.	Fathoms.	Miles.
		= 12ins.	= 3ft.	= 6 ft. =	= 1760 yds.
Millimetre	*03937	'0032809	*0010936	10005468	0000006
Centimetre	*39371	*0328090	0109363	*0054682	10000062
Decimetre	3.03708	*3280899	1003633	'0546816	'0000621
Metre	39.37079	3.2808092	1,0036331	*5468165	'0006214
Decametre	393'70790	32 8089920	10,0363310	5.4681655	'0062138
Hectometre	3937'07900	328.0899200	100.3633100	54.6816550	*0621382
Kilometre	39370'79000	3280'8992000	1003.6331000	546.8165500	6213824
Myriometre	393707'90000	32808 9920000	10936,3310000	5468*1655000	6.2138244
	1		1 0		

ı inch = 2.539954 centimetre. ı yard = .91438348 metre. ı foot = 3.0479449 decimetre. ı mile = 1.6093149 kilometre.

#### Measures of Surface.

	Square Feet.	Square Yards. =9 sq. ft. =	Poles.	Roods. 10,890 sq. ft.	Acres. 43,560 sq. ft.
Centiare or sq. metre	10.7642993	1.1060333	°039 <b>53</b> 83	*000988457	'000 2471143
Are or 100 }	1076'4299342	119'6033260	`3*9538290	*098845724	'0247 <b>1</b> 143 <b>10</b>
Hectare or 10,000 sq. mtrs.	107642*9934183	11960'3326020	395*3828959	9.884572398	2*4711430996
	h = 6.4513669 s oot = 9.2899683	q. centimetres. sq. decimetres.	ı sq. yard = ı acre =	- 83609715 s 4 404671021 h	q. metre. ectare.

### MEASURES OF CAPACITY.

	Cubic Inches.	Cubic Feet.	Pints.	Gallons.	Bushels.			
		=1728 c. in	.=34.65923 c.	in.=8 pints.	=8 gallons.			
Millilitre or c	ubic							
centimetre	°061027	*0000353	.001261	'00022010	'000027512			
Centilitre	.610221	*0003532	017608	*00220097.	000275121			
Decilitre	6.102202	'0035317	176077	'02200997	002751208			
Litre	61.027052	'0353166	1.760763	122009668	027512085			
Decalitre	610 270515	*3531658	17.607734	2.20096677	275120846			
Hectolitre	6102,70212	3.2316281	176.077341	22.00966767	2.751208459			
Kilolitre	61027'051519	35'3165807	1760'773414	220.09667675	27 512084594			
Myriolitre	610270.212194	353'1658074	17607.734140	2200.96676750	275.120845937			
1 cubic in	1 cubic inch=16'3861759 cubic centimetres. 1 cubic foot=28'3153119 cubic							
	deciletre	es. 1 gallon	=4.543457969	litres.	30 3			

#### Measures of Weight.

	Grains.	Troy Ounces. =480 grs.	Avoirdupoi Pounds. = 700 grs.	Cwts.	Tons.
	'015432	.000032	*0000022	'00000002	1000000001
Centigram	154323	1000322	'0000220	'00000020	'000000010
Decigram	1*543235	003215	'0002205	'00000197	*000000008
Gram	15.432349	.032121	10022046	400001968	1000000084
Decagram	154.323488	321507	0220462	'00019684	000009842
Hectogram	1543.234880	3'215073	12201621	00106841	0000098421
Kilogram	15432'348800	32'150727	2.5016513	.01008115	000081206
Myriogram	154323.488000	321.207267	22.0462126	:9684118	009842059

ı grain = '06479895 gram. ı lb. avoirdupois = '45359265 kil. ı ounce troy = 31'103496 ,, ı cwt. = 50'80237689 kil.

### Tables for the conversion of Grammes (or Cubic Centimetres) into Ounces and Grains.

Conve	CONVERSION OF GRAMMES INTO GRAINS.					Conversion of Grains into Grammes.				
Grammes.		O KAII	3,	C	C	GRAM	MES.			
Grammes.				Grains.	Grains.			Grai	nmes.	
I	• • • •		•••	15'43	I				*0648	
2				30'86	2				1296	
3	• • •	• • • •		46.29	3				1944	
4	• • • •	• • • •		61.73	4			•••	'2592	
5	• • • •			77'16					3240	
6	•••	•••	• • •	92'59	6				*3888	
7	•••	•••	• • • •	108.03					4536	
8	• • • •			123'46	8				'5184	
9	• • •			138.89	9				'5832	
Convei		of G		ES INTO	Convers: Avoi		GRAMME OUNCE		0	

						OTICE	1010	OHOL	٥.
Grammes	i•		Tr	oy ounces	Grammes.		Avo	irdup	ois ounces.
ı	•••	•••		'03215	I				'03527
2	• • • •		• • •	'06430	2				'07054
3				109645	3			• • •	'10581
4	• • • •	•••		12860	4	• • •			'14108
5	•••	•••	•••	•16075	5		•••		17635
6	• • • •		• • • •	'19290	6				'21162
7	•••	• • • •	•••	*22505	7	•••		•••	*24689
8	•••	• • • •		*25720	8	•••	• • • •		'28216
9	• • • •	• • • •	• • • •	<b>'2</b> 8935	9	•••	• • • •	•••	*31743

The above tables render the conversion of the weights in question a matter of great ease, the error introduced in the last decimal

place being trivial.

The use of the tables will be best illustrated by an example. Supposing that it is desired to find the equivalent in grains of 324 51 grammes, we proceed by breaking up this number into the following series of constituent parts, and finding the grainequivalent of each part from the table.

Portions of ori	ginal n	umber	r.					Eq	uivalent in grains.
300.				• • • •			•••	•••	4630.
20'						• • • •			308 6
4			•••						61.23
.20					• • •				7716
.01	• • • •								1524
									5008:T081

The required quantity is 5008 2 grains. The numbers taken from the table will, in most cases, require a change as regards the position of the decimal point; thus, to find the value of 300 grammes, one refers to the table and finds 46:30 given as the equivalent, and a mere shifting of the decimal point two places towards the right multiplies this by 100, or gives the required number. In a similar manner, by shifting the decimal place of 30:86 one place to the right we obtain the value in grains of 20 grammes, while the number 61 7 is taken from the table without alteration as the equivalent of 4 grammes. For 50 the table number must have its point shifted to the left, making it 7:716 instead of 77:16, and finally the value of 01 is obtained by shifting the point of 15:43 two places to the left.

The above operations are, in actual practice, performed with considerable speed, the required equivalents being written down one after the other on a scrap of paper, and then added up.

### Thermometric Tables.

Showing the Assimilation of the Thermometers in Use Throughout the World.

Celsius.	Réaumur.	Fahrenheit.	Celsius.	Réaumur.	Fahrenhei
100	80.0	212.0	49	39.5	120.2
	79'2	210'0	48	38.4	118.4
9 <b>9</b> 98	78.4	208'4	47	37.6	116.6
97	77.6	206.6	46	36 8	114.8
97 96	<b>76</b> .8	204'8	45	36°o	113'0
95	76.0	203 0	44	35'2	111.2
94	75'2	201.5	43	34.8	109'4
93	74.4	199'4	42	33 6	107.6
93	73 6	197.6	41	32.8	105.8
91	72.8	195.8	40	32'0	104'0
90	72.0	101.0	39	31'2	102,3
80	71.2	192 2	38	30'4	100'4
89 88	70.4	190'4	37	29.6	98.6
80	69.6	1886		28 8	96.8
87 86	68.8	186.8	36	28.0	
00	68.0	185'0	35	27.2	95'0
85 84	67'2	183.5	34		93'2
04	66.4		33	26'4	91.4
83		181'4	32	25.6	89.6
82	65.6	179.6	31	24.8	87.8
81	64.8	177 8	30	24.0	86.0
80	64.0	1760	29	23.5	84.5
79 78	63.2	174'2	28	22'4	82.4
78	62.4	172'4	27	21.6	80.6
77 76	61.6	170.6	26	20.8	788
76	60 8	168.8	<b>2</b> 5	20'0	77.0
75	60.0	167'0	24	19.2	75°2
74	59.3	165 2	23	18.4	73'4
73	58.4	163.4	22	17.6	71.6
72	57 6	191.9	21	16.8	69.8
71	56 8	159.8	20	16.0	68.0
70	<b>5</b> 6 o	128.0	19	15'2	66.3
69	55*2	156'2	18	14'4	64.4
68	54 4	154'4	17	13.6	62 6
67	53 6	1526	16	12.8	60'8
66	528	150'8	15	12.0	59°O .
6 <sub>5</sub> 6 <sub>4</sub>	52.0	149'0	14	11'2	57.2
64	51.2	147 2	13	10'4	55'4
63 62	50'4	145'4	12	9.6	53.6
62	49.6	143.6	II	88	51.8
61	48 8	141.8	10	8°o	50'0
60	48.0	140 O	9 8	7.2	48'2
59 58	47'2	138.5	8	6.4	46.1
58	46.4	136'4	7 6	5.6	44.6
57	45 6	134.6	6	4.8	42.8
56	44.8	1328	5	4.0	41.0
55	44.0	131.0	4	3 <b>.2</b>	39'2
54	43'2	129'2	3	2'4	37'4
53	42'4	127 4	2	1.6	36.2
52	41'6	125'6	I	0.8	33.8
5 <b>t</b>	40.8	123.8	0	0'0	32 O
50	40'0	122'0			,

#### Useful Data.

A sovereign weighs 123.274 grains.

Mint price for gold = £3 17s.  $10\frac{1}{2}$ d. per ounce (standard).

A shilling weighs 87.273 grains.

Mint price for silver = 5s. 6d. per ounce (standard).

A penny weighs 145.83 grains.

A halfpenny measures an inch across.

A seconds pendulum is 39.1393 inches long at London.

#### Refrigerator Mixtures.

Snow or pounded ice. Crystallised calcium chl	oride	• •	$\frac{2}{3}$ 1	parts)	Refrigeration 50°C.
Ammonium nitrate Sodium carbonate Water	••		1 1 1	,, ,,	Refrigeration 45°C.
Potassium nitrate	••		$\begin{matrix} 6\\4\\2\\4\end{matrix}$	;; ;; ;;	Refrigeration 35°C.
Ammonium chloride Ammonium nitrate Sodium sulphate Water	••	•••	3 2 4 9	;; ;; ;;	Refrigeration 30°C.
Sodium sulphate Strong hydrochloric acid	d.	••	$\frac{3}{2}$	,,	Refrigeration 30°C.
Sodium sulphate Ammonium nitrate Dilute nitric acid	••	•••	$\begin{matrix} 6 \\ 5 \\ 4 \end{matrix}$	,, ,,	Refrigeration 30°C.
Water	••	•••	$egin{matrix} 2 \\ 1 \\ 3 \end{matrix}$	,, ,,	Refrigeration 25°C.
Ammonium nitrate	••		$\begin{array}{c} 12 \\ 5 \\ 5 \end{array}$	"	Refrigeration 25°C.
Snow or pounded ice Dilute nitric acid		••	$_{4}^{7}$	"	Refrigeration 25°C.
Ammonium nitrate Water		••	1 1	"	Refrigeration 25°C.
G-14		••	$\frac{3}{1}$	"	Refrigeration 20°C.
Ammonium chloride	••	•••	1 1 3	,,	Refrigeration 15°C.
Woton		••	1 1	,,	Refrigeration 10°C.

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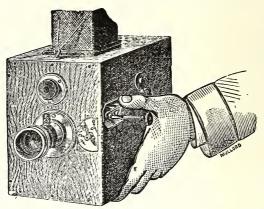
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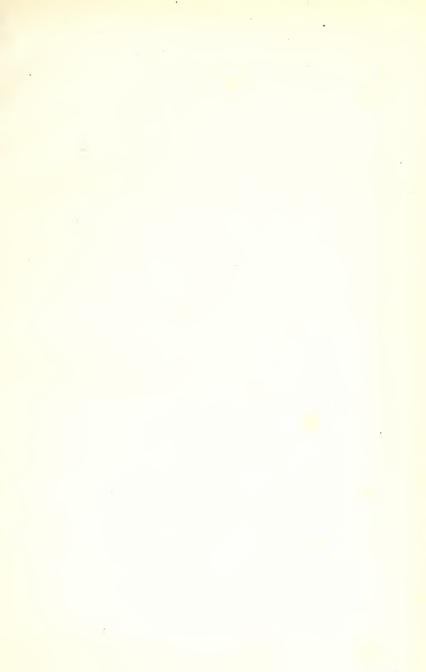
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